Copper complexes of functionalised N-donor ligands

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Copper Complexes of Functionalised *N*-Donor Ligands

submitted by Timothy David Coombs
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Abstract

The primary aim of the research summarised in this thesis was to develop methodologies for producing siloxane-containing reagents of relevance to the catalytic oxidation or hydrolysis of organo-sulfur and -phosphorus materials. Reasons for selecting copper(II) derivatives of acyclic bidentate and cyclic tridentate *N*-donor ligands for these investigations are outlined early in the thesis, mainly by a consideration of the reactivity of thioethers.

The ligands 2,2'-dipydridylamine (Hdpa), bis-(2-methyldipyridyl)amine (Hbmpa) and 1,4,7-triazacyclononane (H_3tacn) were first made suitable for attachment to Si-H units in organosiloxanes by modifying them with *N*-propenyl (Pr) or *N*-pentenyl (Pe) chains to form Prdpa, Pedpa, Prbmpa, Pr_3tacn and Pe_3tacn respectively. The ligand 2-methylamino(*N*-methyl-*N*-2-hydroxyethyl)pyridine, Mamp, which is also suitable for reaction with Si-H units was also prepared. Both Prdpa and Pedpa were successfully hydrosilylated with 1,1,1,3,5,5,5-heptamethyltrisiloxane, Hmts, to form the siloxane supported ligands (Prdpa)Hmts and (Pedpa)Hmts respectively. Attempts to functionalise Hmts with Prbmpa, Mamp, Pr_3tacn and Pe_3tacn were unsuccessful.

A range of $Cu(NO_3)_2$, $CuCl_2$, $Zn(NO_3)_2$ and $ZnCl_2$ complexes of the various *N*-donor ligands were isolated, and the crystal structures of $[Cu(Hdpa)(NO_3)_2]$, $[Cu(Prdpa)_2(NO_3)_2]$, $[Cu(Prdpa)(NO_3)_2]$ and $[Cu(Pr_3tacn)(NO_3)_2]$ were determined. IR and NMR studies of several Zn analogues were also undertaken. The electronic and stereochemical effects of converting the Hdpa ligand to Prdpa were assessed during these studies and showed that *N*-alkenylation can change the primary co-ordination sphere of copper as well as affect the solid state intermolecular interactions. Conditions affecting the disproportionation of $[Cu(Rdpa)(NO_3)_2]$ (R = H or Pr) to $[Cu(Rdpa)_2(NO_3)_2]$ were also explored.

Several poly(dimethylsiloxane) membranes containing known loadings of carbon, silica, $Cu(OH_2)$ or $Zn(OH_2)$ were formed by dispersing the solids in an α,ω-disilanol prior to cross-linking with a poly(hydromethylsiloxane) and tetraethoxysilane. The use of sonication to provide a homogeneous dispersion of solid was briefly investigated.

Acknowledgements

"Education is an admirable thing. But it is well to remember from time to time that nothing that is worth knowing can be taught." – Oscar Wilde.

Bearing this in mind it would seem that after seven years or so of being in full time education I don't actually know anything worth knowing! How much truth there is to that remains to be seen. There are so many people who have helped me in this quest for useless knowledge that it's hard to know where to begin. From the top then are those people that have been the supervisors for this project. Many thanks go to Brian Brisdon without whose guidance and patience none of this would have been possible. Over my years as both an undergraduate and postgraduate student he has always been there to provide invaluable help and suggestions. (He's also able to keep the Manchester United fans in order by constantly reminding them of the result of the 1976 FA Cup Final!) Thanks should also go to Drs. Colin Willis and Stuart Brewer at DERA, Porton Down, without the funding that they supplied there would be no project and without their help and support things would have been a lot harder. Last but not least Dr. Mary Mahon and Mr. Alan Carver for all the crystallography and microanalysis data that they provided me with over the course of this work.

The people that I've worked alongside, and known, over the course of study deserve a big mention here as well, there's quite a few so if I've missed anyone out it's not a deliberate slur it's just my memory isn't what it was. So in no particular order, thanks to Jim (Struthers!) for constant friendship and the absinthe; Mikey (Sumo, Trigger, Cro-magnon Mike, this list is endless!) for showing me how not to write a thesis; Wayne for the booze, birds and bad language; Sam (Elvis) for always being up for a game of pool and a few beers; Tom and the Silver Fox for always being there for a chat to bounce ideas off; Terry and Kermit for the comedy relief; Brian and Julie for providing a bolt hole when things got too much; Chris and G. the best housemates a person could want; David and Nick at the shop for letting me work in a place that has some very happy memories for me; Tim O. at Nashers for the music and being a good friend, and for that matter Sparkle, Rachel, Eloise and Spinner who worked at Nasher's over the years and who helped to keep me sane. Finally, thanks should also go to Elaine, Bruce, Sean, Gav, Paul, Ed, Nathan, Lunster,

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Table of Contents

Abstract ii
Acknowledgements iii
Table of Contents v
Abbreviations Used x
Chapter 1: Introduction 1
1.0 Research Background 3
1.1 Bis-(2-chloroethyl)sulfide, Mustard Gas, HD 5
1.1.1 Physical Properties 5
1.1.2 Synthesis 6
1.1.3 The Chemistry of HD and Other Dialkyl Sulfides 8
1.1.3.1 Nucleophilic Substitution 9
1.1.3.2 S-C Bond Cleavage Reactions 11
1.1.3.3 C-C Bond Cleavage Reactions 12
1.1.3.4 Hydrogen Chloride Elimination from HD 13
1.1.3.5 Oxidation of Di-organosulfides 14
1.1.3.5.1 Stoichiometric Sulfoxidation 14
1.1.3.5.2 Metal Mediated Catalytic Sulfoxidations 19
1.2 Dioxygen Binding by Metal Complexes 24
1.3 Method of Delivery of the Catalytic Agent 30
1.3.1 Heterogenised-Homogeneous Catalysts 32
1.3.2 Organosiloxanes 34
1.3.3 Poly(organosiloxanes) 35
1.3.4 Functionalised Poly(organosiloxanes) 36
1.3.4.1 Hydrosilylation 38
1.3.4.1.1 Radical Initiated Hydrosilyations 39
1.3.4.1.2 Metal Catalysed Hydrosilylations 40
1.3.4.2 Dehydrocoupling 41
1.3.5 Metallation of Linear Organofunctionalised Siloxanes 43
1.3.6 Membrane Formation 46
1.4 Summary 48
1.5 Programme of Research. 49

1.6 References 50
Chapter 2: Acyclic *N*-Donor Ligands and Poly(siloxane) Membranes Containing Dispersed Solids 55
2.0 Introduction 57
2.1 Acyclic *N*-Donor Ligands 57
2.1.1 2,2'-Dipyridylamine, Hdpa 57
2.1.1.1 2,2'-Dipyridyl(*N*-propenyl)amine, Prdpa, 1 59
2.1.1.2 2,2'-Dipyridyl(*N*-pentenyl)amine, Pedpa, 2 60
2.1.2 Bis-(2-methylpyridyl)amine, Hbmpa, 3 62
2.1.2.1 Bis-(2-pyridylmethyl)(*N*-propenyl)amine, Prbmpa, 4 65
2.1.3 2-Methylamino(N-methyl-N-2-hydroxyethyl)pyridine, Mamp, 5 ... 67
2.2 Organofunctionalised Siloxanes 70
2.2.1 Introduction 70
2.2.2 Reactions of Acyclic N-Donor Ligands and Heptamethyltrisiloxane, Hmts 70
2.2.2.1 Prdpa 70
2.2.2.2 Pedpa 72
2.2.2.3 Prbmpa 74
2.2.2.4 Mamp 74
2.2.3 End Group Manipulation 75
2.3 Membranes Containing Dispersed Solids. 76
2.3.1 Carbon and Silica Containing Membranes (11-16) 77
2.3.2 Copper(II) and Zn(II) Hydroxide Containing Membranes (17-23) 78
2.4 Conclusions 80
2.5 References 81
Chapter 3: Cyclic *N*-Donor Ligands 84
3.0 1,4,7-Triazacyclononane, H_3tacn 86
3.0.1 Synthesis of [H_6tacn]Cl_3, 27 86
3.1 The Functionalisation of H_3tacn 90
3.1.1 The Synthesis of Symmetrically N-Functionalised R_3tacn 91
3.1.2 Symmetrically Substituted Alkenyl Derivatives of H_3tacn 92
3.1.2.1 1,4,7-Tri(*N*-propenyl)-1,4,7-triazacyclononane, Pr_3tacn, 28 ... 92
3.1.2.2 1,4,7-Tri(*N*-pentenyl)-1,4,7-triazacyclononane, Pe_3tacn, 29 ... 95

3.1.3 Trisubstituted H_3tacn Containing a Hydroxy-Terminated Alkyl Chain 98
3.2 The Synthesis of Mono-Substituted H_3tacn Derivatives 100
3.3 Attempted Preparation of Cyclic *N*-Donor Ligand Functionalised Trisiloxanes 105
3.3.1 Pr_3tacn and Pe_3tacn 105
3.4 Conclusions 108
3.5 References 109
Chapter 4: The Metallation of Ligands 112
4.0 Introduction 114
4.1 Complexes of Acyclic *N*-Donor Ligands 114
4.1.1 2,2'-Dipyridyl(N-propenyl)amine, Prdpa 114
4.1.1.1 Copper(II) Nitrate 114
4.1.1.1.1 The Crystal Structure of $[Cu(Prdpa)_2(NO3)_2]$, 34 118
4.1.1.1.2 The Crystal Structure of $[Cu(Prdpa)(NO3)_2]$, 35 121
4.1.1.1.3 The Crystal Structure of $[Cu(Hdpa)(NO3)_2]$, 36 124
4.1.1.2 Copper(II) Chloride 128
4.1.1.3 Zinc(II) Chloride 129
4.1.1.4 Zinc(II) Nitrate 129
4.1.2 2,2'-Dipyridyl(N-pentenyl)amine, Pedpa 134
4.1.3 Summary of Complex Formation between Rdpa and $Cu(NO_3)_2$ 135
4.1.4 Structural Comparisons Between Different Cu-Rdpa Complexes 136
4.1.5 Bis-2-methylpyridyl(N-propenyl)amine, Prbmpa, Adduct 139
4.1.6 2-Methylamino(N-methyl-N-2-hydroxylethyl)pyridine, Mamp, Adduct 140
4.2 Complexes of Cyclic *N*-Donor Ligands 141
4.2.1 1,4,7-Tri(N-propenyl)-1,4,7-triazacyclononane, Pr_3tacn 141
4.2.1.1 Copper(II) Nitrate Adduct 141
4.2.1.1.1 The Crystal Structure of $[Cu(Pr_3tacn)(NO3)_2]$, 44 143
4.2.1.2 Zinc(II) Nitrate Adduct 146
4.2.2 1,4,7-Tri(N-pentenyl)-1,4,7-triazacyclononane, Pe3tacn 148

4.2.3 Structural comparison of [Cu(Pr_3tacn)(NO_3)$_2$ with other Cu-R_3tacn Complexes 149
4.3 Conclusions 153
4.4 References 155
Chapter 5: Summary and Further Work. 158
5.0 Introduction 160
5.1 Summary and Implications of the Study 160
5.2 Further Work on Ligand Sytems 162
5.2.1 Acyclic N-Donor Ligands 162
5.2.2 Cyclic N-Donor Ligands 163
5.2.3 Metallation of Ligands 165
5.2.4 Poly(siloxane) Membranes 165
5.3 References 167
Chapter 6: Experimental 168
6.0 General Methods 170
6.0.1 Instrumentation and Solvents 170
6.0.2 Crystallography 171
6.0.3 Starting Materials 171
6.1 General Procedures 172
6.1.1 Organofunctionalisation of Trisiloxanes via Hydrosilylation 172
6.1.2 Membranes Containing Dispersed Solids 172
6.2 Acyclic *N*-Donor Ligands 174
6.2.1 Organofunctionalised Trisiloxanes 177
6.3 Membranes Containing Dispersed Solids 181
6.4 Cyclic *N*-Donor Ligands 181
6.4.1 1,4,7-Triazacyclononane, H_3tacn 181
6.4.2 Symmetrically Substituted H_3tacn Derivatives 184
6.4.3 Asymmetrically Substituted H_3tacn Derivatives 186
6.5 Metal Complexes of *N*-Donor Ligands 187
6.5.1 Complexes of Acyclic N-Donor Ligands 187
6.5.1.1 Cu(II) Adducts of Rdpa (R = H or Propenyl) 187
6.5.1.2 Zn(II) Adducts of Rdpa (R = Propenyl) 189
6.5.1.3 Other Cu(II) Adducts 190
6.5.2 Complexes of R_3tacn (R = Propenyl or Pentenyl) 191

6.6 References 193
Appendix A. Notes on [Cu(Prdpa)$_2$(NO$_3$)$_2$], 34 194
Appendix B: Notes on [Cu(Prdpa)(NO$_3$)$_2$], 35 198
Appendix C: Notes on [Cu(Hdpa)(NO$_3$)$_2$], 36 202
Appendix D: Notes on [Cu(Pr$_3$tacn)(NO$_3$)$_2$], 44 208
Appendix E: Published Work 212

Abbreviations Used

acac	Acetylacetonate anion
Ar	Aromatic
br	Broad
cod	1,5-Cyclooctadiene
CW	Chemical Warfare
d	Doublet
dd	Doublet of Doublets
ddt	Doublet of Doublet of Triplets
DPK	2,2'-Dipyridylketone
DPM	2,2'-Dipyridylmethane
δ	Chemical Shift Value
Et	Ethyl
F_8BINOL	5,5',6,6',7,7',8,8'-Octafluoro-2,2'-dihydroxy-1,1'-binaphthyl
HD	Mustard Gas
Hdpa	2,2'-Dipyridylamine
H_3tacn	1,4,7-Triazacyclononane
IR	Infra-Red Spectroscopy
m	Multiplet
Me	Methyl
NMR	Nuclear Magnetic Resonance
q	Quartet
R	Alkyl
s (IR)	Strong
s (NMR)	Singlet
salen	Bis-salicylaldehydeethylenediimine
t	Triplet
w	Weak

"And if you have five seconds to spare,
then I'll tell you the story of my life...."
- "Half a Person" by The Smiths.

Chapter 1:

Introduction

Chapter 1: Introduction

1.0 Research Background 3
1.1 Bis-(2-chloroethyl)sulfide, Mustard Gas, HD 5
1.1.1 Physical Properties 5
1.1.2 Synthesis 6
1.1.3 The Chemistry of HD and Other Dialkyl Sulfides 8
1.1.3.1 Nucleophilic Substitution 9
1.1.3.2 S-C Bond Cleavage Reactions 11
1.1.3.3 C-C Bond Cleavage Reactions 12
1.1.3.4 Hydrogen Chloride Elimination from HD 13
1.1.3.5 Oxidation of Di-organosulfides. 14
1.1.3.5.1 Stoichiometric Sulfoxidation 14
1.1.3.5.2 Metal Mediated Catalytic Sulfoxidations 19
1.2 Dioxygen Binding by Metal Complexes 24
1.3 Method of Delivery of the Catalytic Agent 30
1.3.1 Heterogenised-Homogeneous Catalysts 32
1.3.2 Organosiloxanes 34
1.3.3 Poly(organosiloxanes) 35
1.3.4 Functionalised Poly(organosiloxanes) 36
1.3.4.1 Hydrosilylation 38
1.3.4.1.1 Radical Initiated Hydrosilyations 39
1.3.4.1.2 Metal Catalysed Hydrosilylations 40
1.3.4.2 Dehydrocoupling 41
1.3.5 Metallation of Linear Organofunctionalised Siloxanes 43
1.3.6 Membrane Formation 46
1.4 Summary 48
1.5 Programme of Research 49
1.6 References 50

1.0 Research Background

Development of new catalytically active species that are efficient, product selective and easy to use is a major research objective in many areas of chemistry. It has become increasingly important in recent years, with the emphasis on so-called "green" (environmentally friendly) chemistry. Catalysis is usually associated with synthesis but is also equally applicable to the decomposition of noxious materials. Thus, if some compounds that are toxic, and very difficult to handle safely, could be catalytically converted to less harmful materials, it would make their disposal far easier and safer. Chemical warfare and nerve agents, many of which have been stockpiled over many years in several countries, are good examples of this. Some of the many of both types of agent are shown in Figure 1.1. Of the chemical agents sulfur mustard is of particular concern because of its ease of preparation and storage and the large quantities thought to be widely distributed around the world.

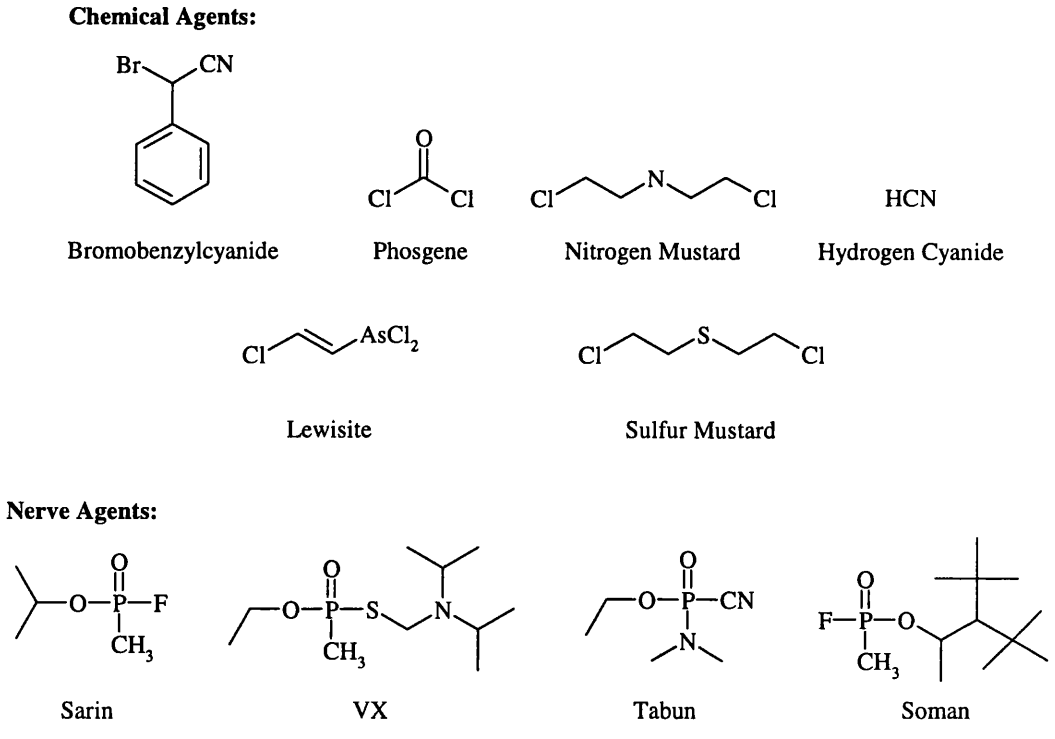


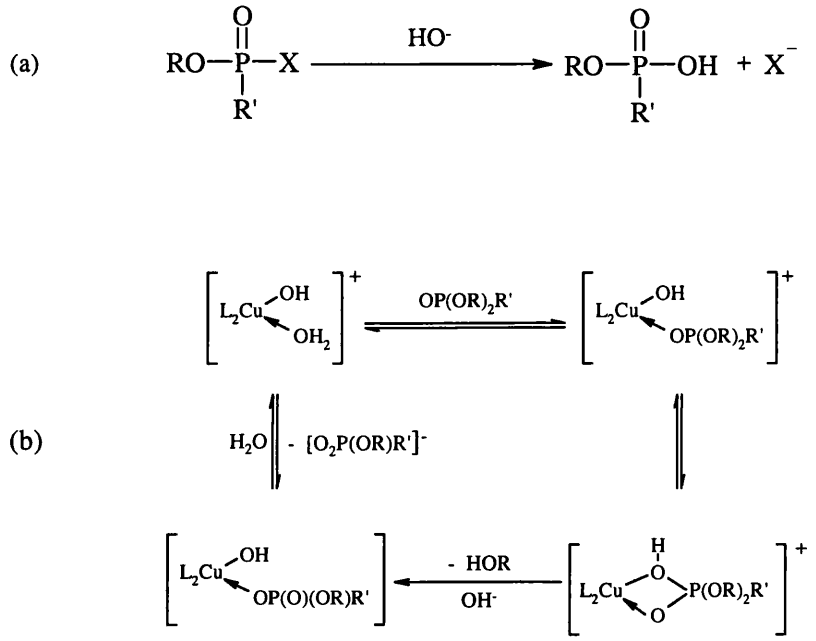
Figure 1.1. Examples of chemical and nerve agents.

As is apparent from the formulae above, most agents have functionalities which are susceptible to oxidation and/or hydrolysis, and bleaching powders based on sodium or

calcium hypochlorite were used initially as general-purpose decontaminants for both chemical and nerve agents.[1] They were used either as powdered solids or in aqueous solution, and react with most of the above agents to produce less or non-toxic products, often in a matter of minutes. Solubilisation of the chemical agent in the same medium as the decontaminant is desirable but not necessary as the reaction can take place at the liquid-liquid interface, for bleach solutions and agents with low water solubility, or at the liquid-solid interface in the case of bleaching powders. Highly chlorinated bleaches were still in use by World War II, but they suffer from a number of significant disadvantages:

- An excess of the bleach must be used for the complete oxidation of agents.
- Bleach is corrosive to many surfaces.
- Bleach converts some agents into compounds that are themselves highly toxic.
- The active chlorine content of the bleach decreases over time, so fresh solutions have to be prepared prior to use.

Sarin and the other organophosphorus nerve agents are particularly reactive, which also means that they are readily destroyed, for example by hydrolysis. By using an excess of aqueous alkaline solutions they can be quickly hydrolysed to the corresponding phosphoric acid or its salt[1], Scheme 1.1(a), and it has been shown that Cu^{2+} in conjunction with bidentate amine ligands,[2,3] are particularly effective catalysts for this type of reaction.[4] The active species in the process shown in Scheme 1.1(b) is the $[CuL_2(OH)(H_2O)]^+$ ion (where L = a bidentate *N*-donor ligand), which promotes the intramolecular attack of Cu-OH on the co-ordinated organophosphate.



Scheme 1.1. Hydrolysis of organophosphates by (a) alkali or (b) Cu(II) derivatives.

This chapter describes the chemistry associated with the decontamination of mustard gas, the method of delivery of decontaminants, and catalytic systems of relevance to these investigations. **Section 1.4** summarises the important aspects of the chemistry under investigation in this study and the direction of research undertaken.

1.1 Bis-(2-chloroethyl)sulfide, Mustard Gas, HD

1.1.1 Physical Properties

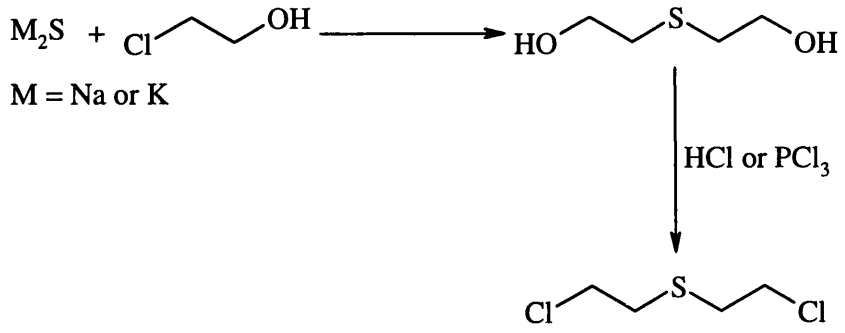
Mustard gas is a toxic liquid (b.p. 216°C) that has a low vapour pressure (0.072 mmHg) at room temperature, and low water solubility (0.68 g dm^{-3} at 25 °C),[5] the medium in which it is most reactive. The low solubility of HD in water can be reduced even further by the addition of some 5% of a polymer (polychlorinated isoprene for example). This "thickener" forms an interface with most aqueous solutions preventing dissolution of the agent, thus slowing any aqueous based detoxification process. The possible use of such a thickener causes constraints in the design of efficient decontamination systems.

The toxicity of HD arises from the fact that it acts as a nucleic acid alkylating agent, and as it is very lipophilic, it is readily absorbed through the skin causing blistering in 6-24 h. It can also affect the eyes, and when inhaled, the respiratory tract.[6] Lung cancers have also been reported in workers at HD manufacturing plants.[6] There is no known drug that is overly effective against the effects of HD and the best protection is avoidance, or immediate decontamination and medical treatment. The low vapour pressure of HD means that it evaporates very slowly, and so it can remain as a contaminant on a surface for hours or even days, depending on ambient weather conditions. Therefore, HD is also a pick-up and transfer hazard, and the vapours evolved over this period can also be hazardous to areas downwind of the contaminated site. Due to its low water solubility, HD also has a very low rate of dissolution in aqueous media at ambient temperatures, which greatly hinders its removal from surfaces.

The decontamination of materials impregnated by HD can be accomplished by using both reactive (chemical) and unreactive methods. Reactive decontaminants are more effective than unreactive ones as they are capable of removing the agent faster, and destroying it completely. Unreactive methods include physical removal of HD based on dissolution, evaporation or absorption. Contaminated surfaces that are decontaminated by scrubbing, spraying with a soap solution or a steam jet, or covering with absorbent materials, merely transfers the problem elsewhere and produces HD contaminated waste, which still requires treatment.

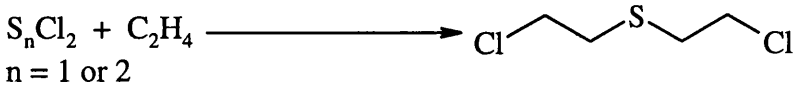
1.1.2 Synthesis

One of the earliest syntheses used for HD was reported by Meyer in 1886 and involved the halogenation of 2,2'-thiodiethanol (which is itself toxic).[7] By treating K_2S with the halohydrin, 1-chloro-2-hydroxyethane, 2,2'-thiodiethanol could be isolated and then further halogenated by treatment with PCl_3 to produce HD. This methodology was improved in 1912 by Clarke, who reported the synthesis of 2,2'-thiodiethanol from Na_2S and the halohydrin followed by quantitative halogenation by aqueous HCl, in an overall yield of *ca.* 94%.[8] Both modifications are summarised in Scheme 1.2 below.



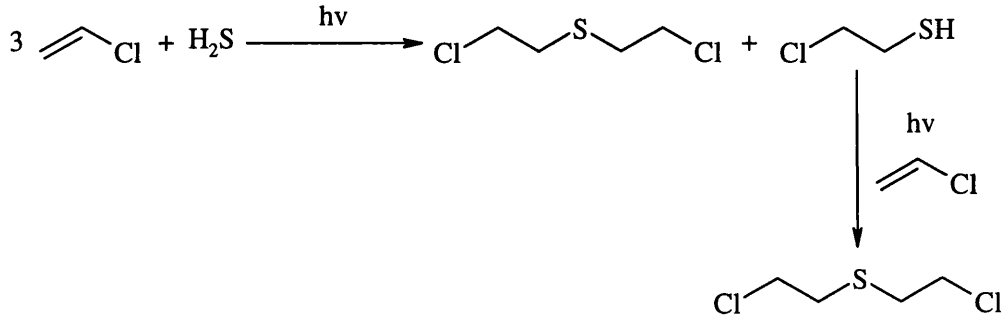
Scheme 1.2. Synthesis of HD from 2,2'-thiodiethanol and hydrogen chloride.

A second synthetic procedure involves treating either SCl_2[9] or S_2Cl_2[10] with a stream of ethylene gas (Scheme 1.3) however overall yields are low in both cases (*ca.* 30%).



Scheme 1.3. Synthesis of HD from sulfur dichloride and ethene.

These two procedures are among the first that were developed for the synthesis of HD although others have been reported over the years, for example, the photolysis reaction between vinyl chloride and hydrogen sulfide as summarised in Scheme 1.4.[11] Both starting materials are readily available, and the side product of this reaction, chloro-ethanethiol, can react further, under photolytic conditions, with another molecule of vinyl chloride to produce another equivalent of HD.[12]



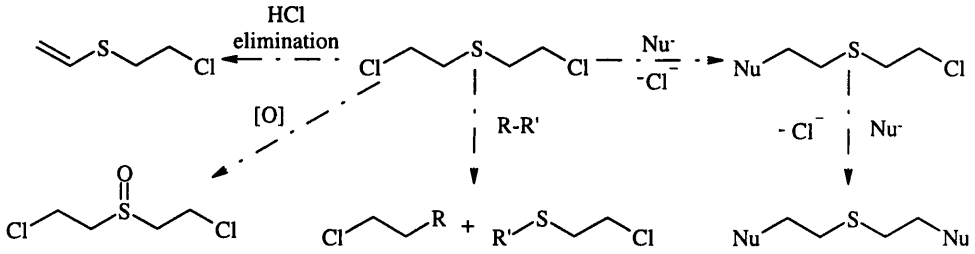
Scheme 1.4. Synthesis of mustard gas from vinyl chloride and hydrogen sulfide.

It is because of the ease and low cost of synthesis, as well as its effectiveness that has made HD an attractive choice of chemical warfare agent for nearly 100 years. However with the advent of international treaties restricting the use of chemical weapons many countries are left with stockpiles that need to be destroyed. Other countries that do not subscribe to these treaties may also have stockpiles of HD and other agents, and so finding new methods of destroying and/or counteracting with exposure to chemical and nerve agents could save lives as well as remove a lingering problem.

1.1.3 The Chemistry of HD and Other Dialkyl Sulfides

As HD is a dialkyl sulfide the known chemistry of these species is relevant in considering how to chemically alter it. Characteristic reactions of HD and several of which are characteristic of dialkyl sulfides are summarised below in Scheme 1.5 and include:

- substitution of the chlorine atoms on the β-carbon atoms by other nucleophiles;[13,14,15,16,17]
- cleavage of the C-S,[18] or C-C[19] bonds;
- elimination of one or both chlorides as HCl to produce vinyl compounds;[1]
- oxidation of the sulfide without bond scission to afford either the sulfoxide (R_2SO), or the sulfone (R_2SO_2).[20]



Scheme 1.5. Different routes for the decomposition of mustard gas.

Another indicator of potentially effective methods for decontaminating HD comes from examining the bond enthalpies in the molecule; these have been determined experimentally and are given in Table 1.1 below.[21] They show that the strengths of the three different bonds in mustard decrease in the order C-C > C-Cl > S-C, but that all three are relatively strong bonds. As it is easier to attack and break the polar C-Cl and S-C bonds, rather than

the C-C bonds, nucleophilic substitution at the β-carbon, or electrophilic substitution at the sulfur centre, provide two possible reactive sites upon which decontamination chemistry can be based. As mentioned previously the central sulfur(II) atom is also susceptible to oxidation thus giving another reaction type.

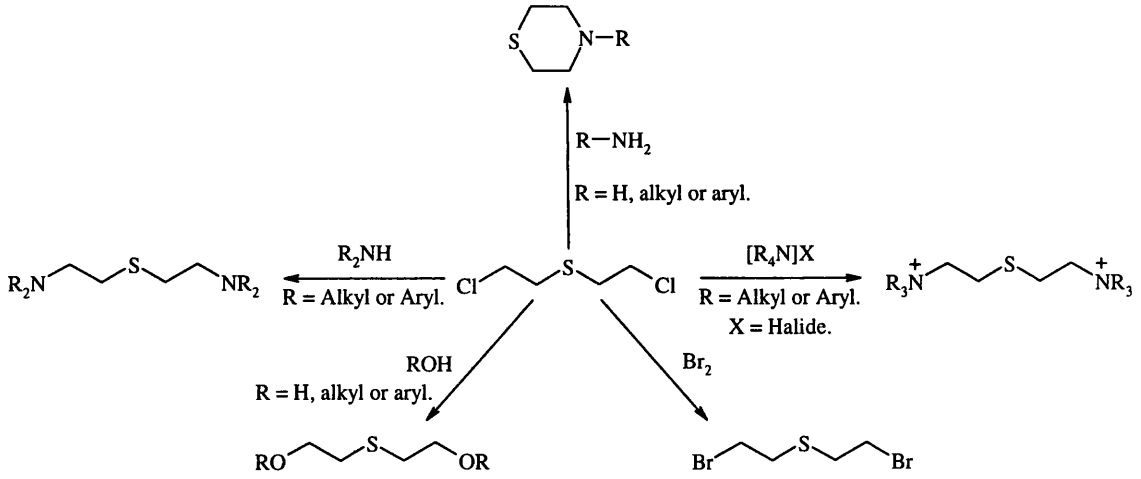
Bond	Bond enthalpies / $kJmol^{-1}$
S-C	320 ± 7
C-C	358 ± 10
C-Cl	343 ± 5

Table 1.1. Bond enthalpies for mustard gas in kJ mol^{-1}.

Each of the different reaction types summarised in Scheme 1.5 above are discussed in more detail in **Sections 1.1.3.1-1.1.3.5** below and are also evaluated for their effectiveness at detoxifying HD.

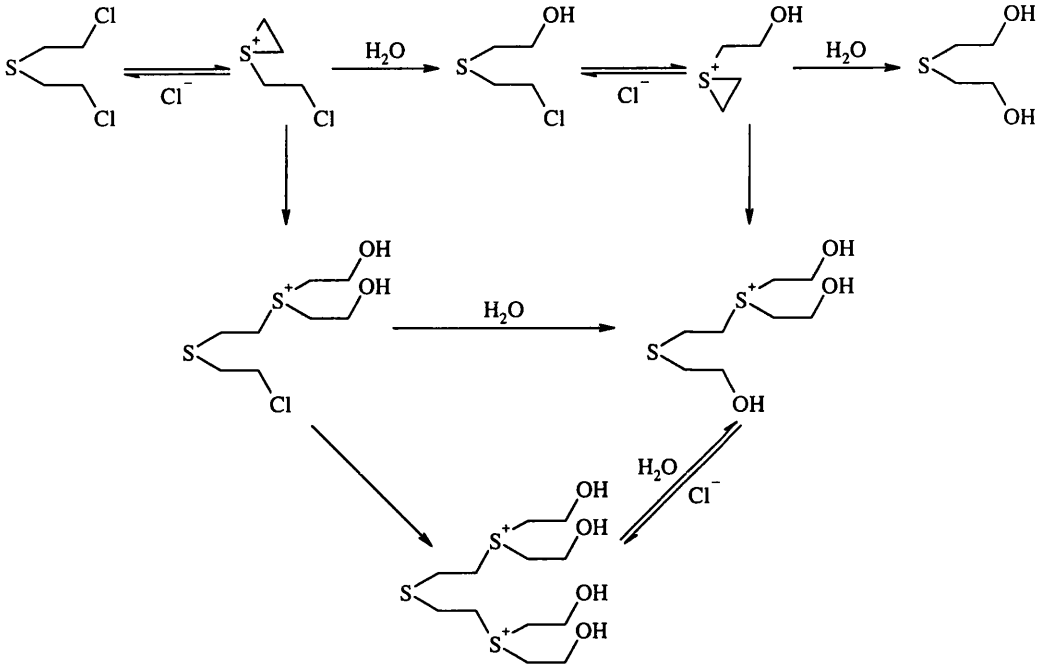
1.1.3.1 Nucleophilic Substitution

Nucleophilic substitution can take place at one or both of the β-carbon atoms of HD. A wide range of nucleophiles can be used to substitute the chloride atoms including primary,[13] secondary[14] and tertiary[15] amines, alcohols[16] and other halogens.[17] Primary amines react with mustard gas to give the corresponding cyclic thiomorpholine product. Secondary and tertiary amines, as well as alcohols and other halides, replace both chlorides generating linear products as shown in Scheme 1.6.



Scheme 1.6. Nucleophilic substitution at the β-carbons of mustard gas.

HD can also be hydrolysed and this occurs *via* series of reversible reactions as shown in Scheme 1.7 below.[1] The mechanism for this reaction has been determined as being S_n1[22] and the rate of dissolution of HD in aqueous solutions, at ambient temperature, is extremely slow and rate determining. Initially the loss of a chloride ion from HD allows the formation of a cyclic ethylenesulfonium ion intermediate. This is then ring opened by a molecule of water to form the mono-hydroxylated compound. A similar process follows the loss of the second chloride to form 2,2'-thiodiethanol. Further studies on this hydrolysis showed that sulfonium aggregates are also reversibly formed in this process, and these can further decompose to regenerate HD.[23] The product formed by the hydrolysis of HD, 2,2'-thiodiethanol, as mentioned previously is itself toxic and also a starting material in the synthesis of HD. This makes reaction with water alone under normal conditions an ineffective method for detoxifying HD.

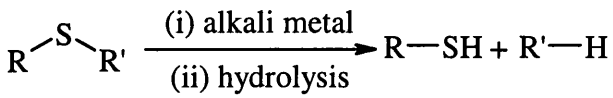


Scheme 1.7. Stepwise hydrolysis of HD and formation of sulfonium aggregates.[1]

The other nucleophilic substitution reactions illustrated in Scheme 1.6 all require long reaction times and forcing conditions. These limitations make this general route unfeasible for decontaminating surfaces for example but could have applications for the disposal of HD.

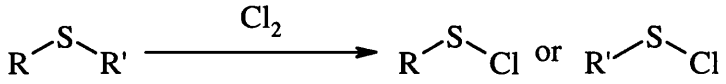
1.1.3.2 S-C Bond Cleavage Reactions

The synthesis of thiols from dialkyl- and diaryl sulfides is a general laboratory-based transformation that utilises S-C bond cleavage reactions. On reaction of a symmetrical di-aliphatic sulfide with sodium, or other alkali metal, the corresponding thiol is produced after hydrolysis, according to the reaction given in Scheme 1.8 below. This methodology is not considered further as it has no practical application in decomposing HD under atmospheric conditions.



Scheme 1.8. Formation of a thiol from a sulfide.

A S-C bond cleavage reaction also occurs on chlorination of an organic dialkyl or diaryl sulfide.[18] This reaction leads to the formation of a S-Cl bond and has been performed on HD, Scheme 1.9.[24] However, it has limited usefulness outside of the laboratory as it requires stoichiometric amounts of Cl_2, which is itself a toxic gas used previously in chemical warfare. A similar reaction occurs with pseudohalogens such as CNBr, leading to the formation of an organic thiocyanate.[25]

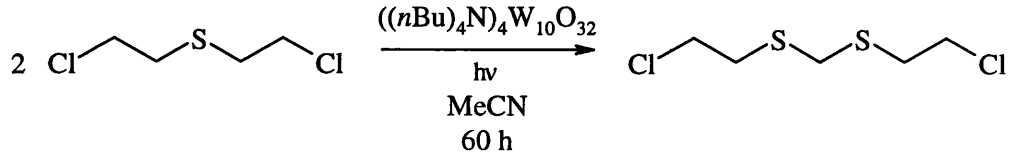


R = alkyl, aryl or $(CH_2)_2Cl$
R' = alkyl, aryl or $(CH_2)_2Cl$

Scheme 1.9. The chlorination of sulfides.

1.1.3.3 C-C Bond Cleavage Reactions

As was noted previously (Table 1.1) the cleaving of any of the bonds in HD is a highly energetic process. The overall stability of C-C bonds in general makes them difficult to activate, and so such reactions would require forcing conditions. A rare example of a C-C cleavage reaction applied to HD involves its irradiation over 60 h in MeCN in the presence of a tungsten oxide cluster, Scheme 1.10.[26]

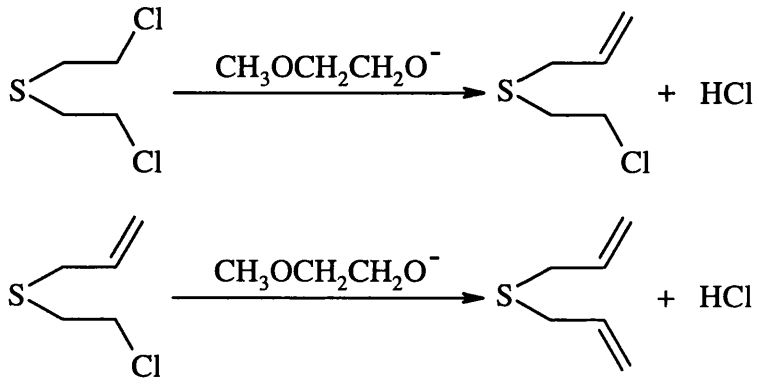


Scheme 1.10. C-C bond cleavage of HD.

Because of the greater reactivity of other parts of the HD molecule, it seems unlikely that reactions involving C-C bond cleavage will provide a viable, practical route to HD decontamination procedures.

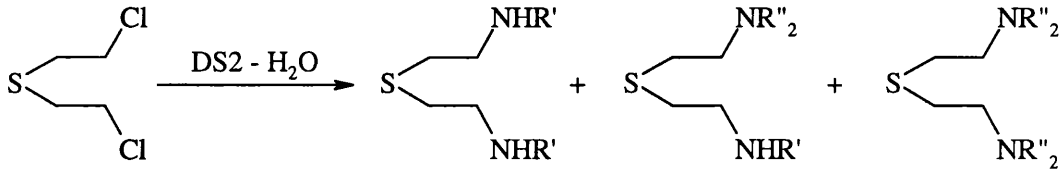
1.1.3.4 Hydrogen Chloride Elimination from HD

The final non-oxidative reaction of HD considered in Scheme 1.5, involves HCl elimination and the formation of vinyl derivatives. This can be achieved under alkaline conditions and forms the basis of an alternative procedure to bleaching agents for the decontamination of HD and the phosphorus based nerve agents.[1] A combination of 70% diethylenetriamine, 28% ethylene glycol monomethyl ether and 2% sodium hydroxide by weight, designated DS2, was developed for use after World War II. The active component of DS2 was found to be the conjugate base of ethylene glycol monomethyl ether, which instantaneously reacts with HD, at ambient temperatures, to form the corresponding divinyl compound, Scheme 1.11. The mono-vinyl compound shown in Scheme 1.11 is a proposed intermediate, which has not been observed due to the speed and efficiency of this reaction.



Scheme 1.11. HCl elimination from HD on reaction with DS2.[1]

On exposure to air or large quantities of water the active conjugate base is reprotonated, and instead of HCl elimination occurring, the nucleophilic substitution of diethylenetriamine for the terminal chlorides of HD happens, Scheme 1.12.



Scheme 1.12 Reaction of DS2 with HD in the presence of excess water.[1]

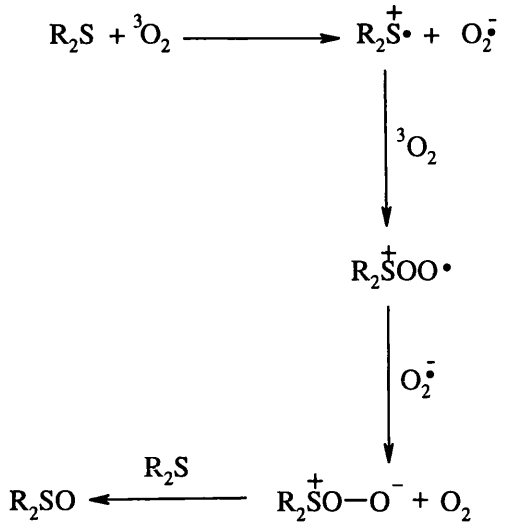
This system has a major advantage over bleaching agents in that being non-aqueous the low water solubility of HD is not a problem. DS2 is also non-corrosive to metal surfaces and can be stored for longer periods. However on prolonged exposure paints, plastics, rubber and leather are damaged. The handling of DS2 is also hazardous, and requires the use of breathing apparatus, eye shields and chemically-resistant gloves, as it is corrosive on contact with skin. Whilst DS2 is an efficient decontaminant its hazardous nature is an undesirable feature.

1.1.3.5 Oxidation of Di-organosulfides.

There are numerous catalytic and stoichiometric reagents capable of oxidising dialkyl sulfides and it is also a relatively easy reaction to perform.[27] The interconversions of sulfide ↔ sulfoxide ↔ sulfone can all be performed reversibly with the exception of the sulfone to the sulfoxide reduction. In this section an overview of the different stoichiometric and catalytic methods that have been used to affect sulfoxidation reactions of dialkyl, diaryl and alkyl-aryl sulfides, as well as HD, is presented.

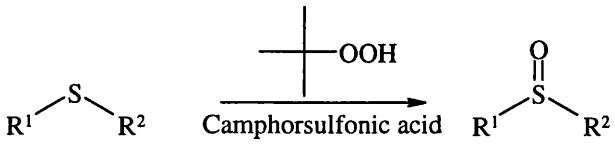
1.1.3.5.1 Stoichiometric Sulfoxidation

The oxidation of R_2S compounds (where R = alkyl or aryl) to the corresponding sulfoxide using O_2 as the oxidant, is a very slow process and has been recorded as going to completion only after a number of days under vigorous conditions (100°C and 1000 psi O_2 pressure).[28] The mechanism for this reaction, summarised in Scheme 1.13, is thought to involve initially the energetically unfavourable electron transfer from the sulfide to molecular oxygen, thus producing a superoxide. Excess O_2 (in the triplet ground state) then traps the organic radical cation, which then accepts an electron from the superoxide to yield a zwitterionic species. This in turn affords the sulfoxide on exposure to additional diorganosulfide.



Scheme 1.13. Oxidation of a sulfide by O_2.

It is possible to use acid catalysis to facilitate this oxidation reaction. Using *t*-butyl hydroperoxide as the stoichiometric oxidant and a catalytic amount (10%) of camphorsulfonic acid, it was found that a range of dialkyl and diaryl sulfides could be oxidised to the corresponding sulfoxides in good yields (95-100%) with little or no sulfone production, Scheme 1.14.[29] Although suitable for the laboratory conversion of dialkylsulfides to the corresponding sulfoxide, this methodology is of no direct use for practical HD decontamination purposes.

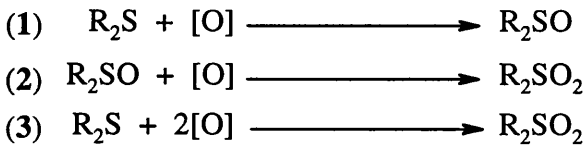


R^1 = Ph, R^2 = Me
R^1 = Ph, R^2 = Ph
R^1 = *p*-ClC_6H_4, R^2 = Me
R^1 = *p*-tolyl, R^2 = Me
R^1 = R^2 = *n*-Bu
R^1 = *t*-Bu, R^2 = Me

Scheme 1.14. Acid catalysed oxidation of a range of sulfides to sulfoxides using *t*-butyl hydroperoxide.

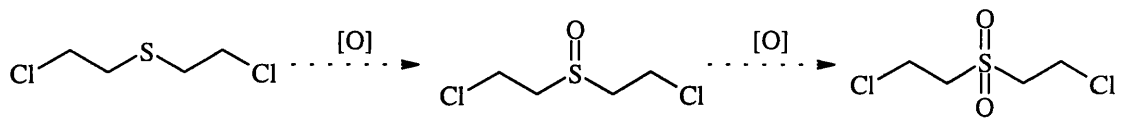
Oxidation of the sulfoxide to sulfone by other oxidants is often difficult to prevent, especially in the presence of an excess of the oxidant. There are three competing reactions

to consider as shown in Scheme 1.15.[30] Depending on the oxidant used **Equation 2** can occur at a faster rate than **Equation 1**, so as soon as the sulfoxide is produced it is consumed to form the sulfone. This behaviour is typified by two reactions. The stoichiometric oxidation of sulfides by RuO_4, as reported by Djerassi and Engle, leads to nearly quantitative production of the sulfone, with little of the intermediate sulfoxide being isolated.[31] Whereas, the investigations of Henbest and Khan showed that diaryl sulfides were oxidised more slowly to the sulfoxide by the $[MnO_4]^-$ anion, than the corresponding diaryl sulfoxides were oxidised to the sulfone.[32] For example only 3% of dibenzyl sulfide was oxidised by $[MnO_4]^-$, after 5 mins at 20°C. Under the same conditions the sulfoxide is converted to the sulfone nearly quantitatively (>95%). However if sodium periodate is used as the oxidant, dibenzyl sulfide is converted to the sulfoxide in 96% yield, with very little sulfone production.[33] **Equation 3**, although rare, is also a possible reaction pathway for the direct formation of the sulfone with no intermediate sulfoxide formation. Therefore, an important aspect of oxidative decontamination is to be able to maintain a precise degree of control over the reaction to prevent sulfone formation, or to effect its further degradation if formed.



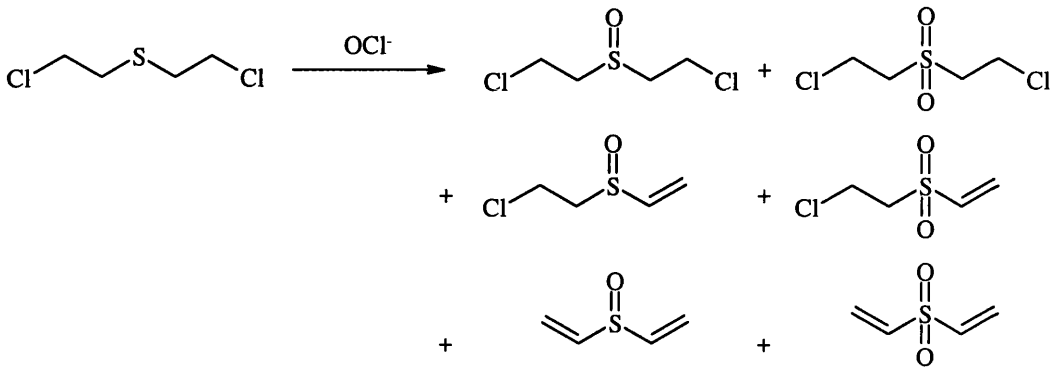
Scheme 1.15. Reaction pathways for the oxidation of dialkyl sulfides.

Oxidising the sulfur atom of HD from S^{2+} to S^{4+} creates the sulfoxide derivative, which is non-toxic, but further oxidation to S^{6+} will produce the corresponding sulfone, which is nearly as toxic as mustard gas itself, Scheme 1.16. Despite the possibility of sulfone formation, HD oxidation has been in the past, and remains, the most attractive route for HD decontamination procedures.



Scheme 1.16. Oxidation of mustard gas to its sulfoxide and sulfone derivative.

As noted above for general laboratory based procedures, the conversion of a sulfide to the corresponding sulfoxide can be performed using a large number of stoichiometric reagents. Of these sodium and calcium hypochlorites were chosen as the first practical oxidants to be used for HD decontamination. It is considered that first the sulfoxide then the sulfone is formed. Subsequently both of the oxidation products undergo elimination in the strongly basic solution to form mainly mono- and di-vinyl sulfoxides and sulfones, Scheme 1.17.[1]



Scheme 1.17. Oxidation of HD using the hypochlorite ion.

As previously noted, although mustard gas has low water solubility it is also highly reactive in aqueous solution. One method that has been used to solubilise mustard gas in water relies on surfactant chemistry and microemulsion formation.[34] A microemulsion prepared from a hydrocarbon, a surfactant, and a low molecular weight alcohol, Figure 1.2 is able to solubilise the organophilic HD analogues (2-chloroethyl)ethylsulfide and (2-chloroethyl)(2-phenylethyl)sulfide (also known as "half mustards"). These are used as models for HD as they are less toxic and therefore easier to handle, and in this study were found to have increased reactivity towards oxidation and hydrolysis.

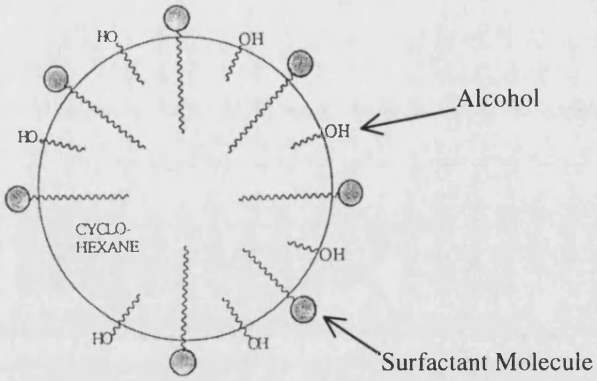


Figure 1.2. Formation of a micelle in aqueous media.

It was reported by Menger and Elrington that by using a micro-emulsion, containing 1-butanol as the co-surfactant, the half-mustards were quickly and completely oxidised to the corresponding sulfoxide using hypochlorite as the stoichiometric oxidising agent, Figure 1.3.[35] Under these conditions the reaction is complete in *ca.* 15 s, and occurs much too quickly for the recording of kinetic data. When no co-surfactant is present the reactions were still incomplete after 5 h. It was proposed that on addition of hypochlorite to the micro-emulsion, the alcohol reacts to form an alkyl hypochlorite which acts as the active oxidant at the oil/water interface, Figure 1.3. Whilst this method is not catalytic, it is very practical, fast and quite cheap. Commercial bleach was used as the source of hypochlorite in this investigation, but as already mentioned it too is quite a corrosive chemical.

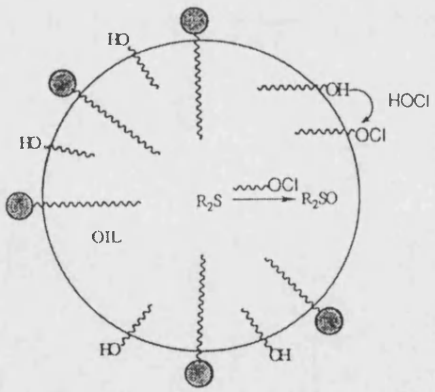


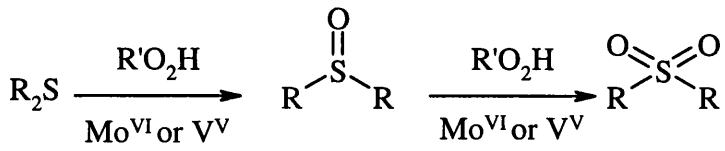
Figure 1.3. Oxidation of "half-mustard" in a microemulsion.

1.1.3.5.2 Metal Mediated Catalytic Sulfoxidations

There have been many investigations on different metal-containing systems capable of catalytically oxidising sulfides to sulfoxides. Most of these studies have been concerned with the formation of more synthetically useful sulfoxides rather than the decontamination of HD. A selection of these more general methods, to show the range of ligand-metal combinations that can be used for this reaction, as well as specific HD sulfoxidations, are described below.

First row transition metal derivatives of macrocycles feature prominently in catalytic oxidations of organic sulfides, as illustrated in the early examples below.

In the presence of H_2O_2, or an alkylperoxide, and a metal catalyst, usually containing molybdenum or vanadium, the oxidation of a sulfide to the corresponding sulfoxide occurs.[36] If the peroxide is present in excess, oxidation proceeds directly to the sulfone, Scheme 1.18.



R = alkyl or aryl
R' = H or alkyl

Scheme 1.18. Catalytic oxidation of an alkyl sulfide to its sulfoxide and sulfone derivatives.

This reaction proceeds *via* one of two pathways. Either a metal-peroxo or a metal oxo species are formed which then oxidise the substrate, Figure 1.4.[37] Metal-oxo species are usual intermediates in reactions catalysed by late or first row transition metals, whereas metal-peroxo species are active in reactions where early transition metals with a d^0 configuration provide the catalytic species.[38] Both V^{5+} and Mo^{6+} have a d^0 electronic configuration, but the former is more likely to catalyse reactions through the metal-oxo species than the latter.[38]

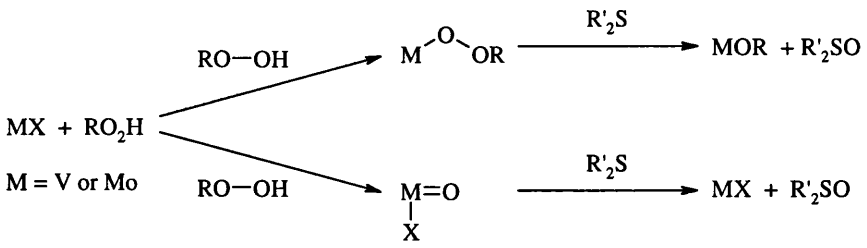
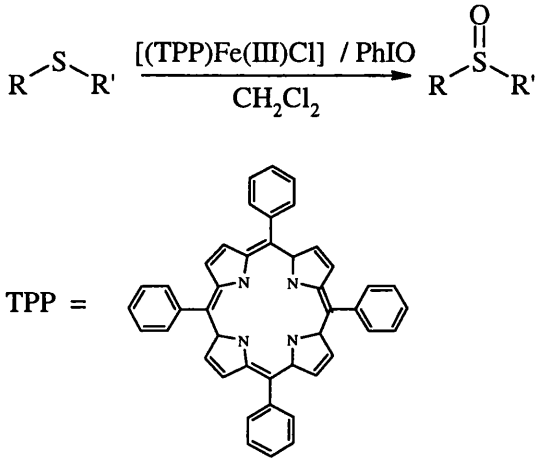


Figure 1.4. Mechanisms of V^{5+} and Mo^{6+} metal catalysed oxidations.

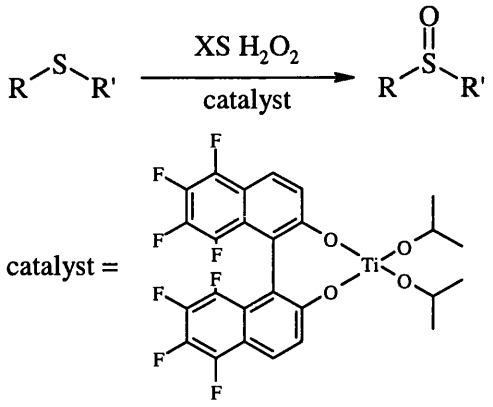
Metalloporphyrins have been studied as models for the active intermediates in the catalytic oxidation cycles of peroxidase enzymes as well as cytochrome P-450.[39] Both dialkyl and diaryl sulfides can be oxidised to the corresponding sulfoxides, using an iron(III) tetraphenylporphyrin catalyst with iodosylbenzene as the oxidant.[40] The yields of sulfoxide ranged from between 77-94% depending on the substrate, with no detectable sulfone production in most cases. An exception found in this study was dibenzyl sulfoxide, which was converted to the corresponding sulfone in 95% yield.



Scheme 1.19. Sulfoxidation catalysed by a [(TPP)Fe(III)] based catalyst.

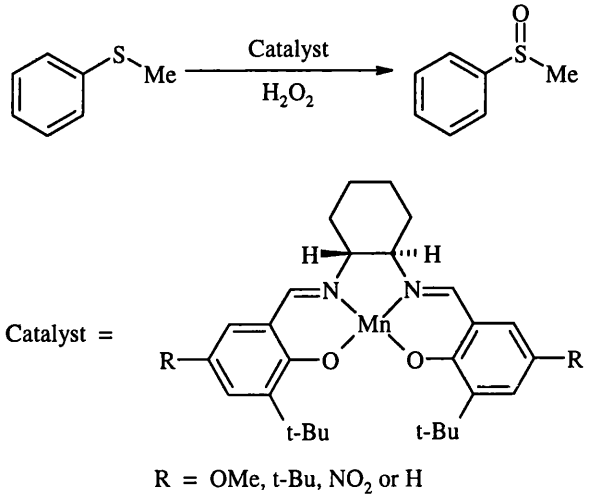
The fluorinated ligand F_8BINOL will complex with titanium(IV) isopropoxide to form a catalyst that, in the presence of H_2O_2, will oxidise a range of thio-ethers to their corresponding sulfoxides, Scheme 1.20.[41] The reaction occurs under mild conditions at temperatures varying between -20°C to room temperature. Yields are substrate dependent and vary from 55-75% after an 18 h reaction period. Although specific to sulfoxide

formation, the low yields and long reaction times make this process unsatisfactory for the "on-site" decontamination of HD.



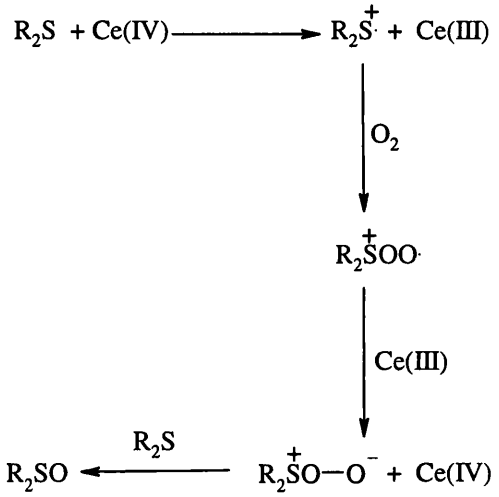
Scheme 1.20. F_8BINOL catalysed sulfoxidation reactions.

The salen group of ligands have also played a prominent role in sulfoxidation catalysis. Various metal complexes of these tetradentate Schiff base ligands containing vanadium,[42] titanium[43] and manganese,[44] have been employed to facilitate the enantioselective sulfoxidation of different sulfides to sulfoxides, using alkyl hydroperoxides, or H_2O_2, as the terminal oxidant.[44,45] The sulfoxidation of thioanisole by H_2O_2 was studied using various [Mn(salen)] based catalysts, Scheme 1.21. It was found that yields of the sulfoxide varied from between 64-90%, after 1 h at room temperature, with only minimal sulfone formation in all cases.



Scheme 1.21. Sulfoxidation using a Mn(salen) based catalysts.

As shown in Scheme 1.13 the slow oxidation of sulfides to sulfoxides takes place *via* an unfavourable electron transfer step. It was found that by using the one electron oxidant, ceric ammonium nitrate (CAN), this reaction can be performed catalytically.[28] The initial conversion of the sulfide to the radical cation (Scheme 1.13) is performed by Ce(IV), which is reduced to Ce(III). The radical cation of the sulfide then reacts with O_2 to form the oxygenated radical as shown previously. This is then reduced to the zwitterionic species by Ce(III) with reformation of Ce(IV). Once this zwitterionic species is formed the reaction proceeds as before, Scheme 1.22. However, this reaction requires prolonged reaction periods (from 30 mins to 5 h) at elevated temperatures and a positive pressure (14 bar) of O_2.



Scheme 1.22. Ce(IV) promoted sulfoxidation.

Hay and Govan reported the oxidation of both di(*n*-butyl)sulfide and HD by *tert*-butylperoxide using several of the types of transition metal catalyst highlighted above, but in microemulsions composed of either of the non-ionic surfactants BRIJ 97® or SD2®.[46] In the presence of the manganese catalyst, $[Mn_2(Me_3tacn)_2(MeCO_2)_2(\mu\text{-}O)](ClO_4)_2]$ (Me_3tacm = 1,4,7-trimethyl-1,4,7-triazacyclononane), oxidation of the sulfide to the sulfone is observed. However, when a vanadium catalyst, $[VO(acac)_2]$ was used in conjunction with the peroxide only the sulfoxide was formed, Figure 1.5.

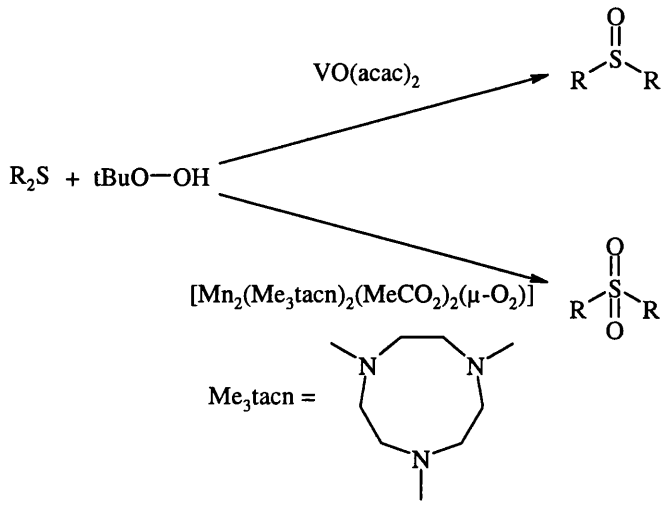


Figure 1.5. Sulfoxidation using Mn and V based catalysts.

The use of various polyoxometallates (POMs), in conjunction with alkyl peroxides, to affect the catalytic sulfoxidation of HD has also been investigated.[19,47-49] POMs containing vanadium, molybdenum or tungsten or various combinations of these three, catalyse oxidations by one of five homogeneous modes depending on the nature of the POM. The first two modes described below being the most common.[47,48]

- The HPA directly oxidises the substrate and is then itself reoxidised by a terminal oxidant.[47]
- The POM functions as a co-catalyst with other metallic species, for example palladium in Wacker oxidations.[48]
- The POM catalyses oxo transfer from the terminal oxidant to the substrate.[49]
- The POM photocatalyses the oxidation.[19,50]
- The cation of the polyanion activates and oxidises the substrate.[51]

These species are of interest as they have been immobilised in porous carbon materials and used as heterogeneous catalysts.[52] Thus, the HPA [$H_5PV_2Mo_{10}O_{40}$] catalyses the oxidation of tetrahydrothiophene, using *tert*-butylhydroperoxide as the oxidant, to the corresponding sulfoxide, at room temperature with a very high selectivity (>99.99%).**Error! Bookmark not defined.** By supporting this material on porous carbon, the reaction still occurs at room temperature with only a minor loss of selectivity.[52]

In all of these examples, the metal species acts as a true catalyst, but the reaction requires an external oxidant, which is normally present in excess, and is frequently a peroxide. Although useful for laboratory transformations, such oxidants are hazardous and impractical for many decontamination applications. An efficient catalytic species that can perform the HD sulfoxidation reaction and does not rely on peroxides as the oxidant, but rather utilises molecular oxygen, O_2, either as the oxidant, or to re-oxidise a reduced metal centre, would be easier to handle and have more general applications. Molecular oxygen itself is rather unreactive at ambient temperatures and needs to be activated in some way to form a more reactive species. The manner in which this is achieved by transition metal containing species is described in the following section.

1.2 Dioxygen Binding by Metal Complexes

The oxygenation of organic substrates by oxygenase enzymes utilises molecular oxygen directly. Such reactions should also be possible using synthetic mimics of these enzymes. In order to reproduce effectively the enzymatic reaction pathway in the laboratory the metal complex must be able to activate dioxygen in a similar manner. This is usually achieved by enzymes *via* a $M_n(O_2)$ transition state (n = 1 or 2 depending on the enzyme in question) but to date it has proved difficult to model these transition states accurately in most cases. Instead O_2 in the presence of active transition metal complexes mainly reacts with organic substrates *via* a free-radical mechanism. Another important feature of metalloenzymes is the restrictive nature of the protein chain, which creates an appropriately sized cavity for the active site to accommodate and activate O_2. Therefore, in order to effectively model metalloenzymes in the laboratory various ligand systems with substituents which can sterically "crowd" the metal centre, have been investigated.[53,54]

One of the metals that have undergone intense investigation in the area of biomimetic catalysis is copper. Complexes with one or more copper centres are found in many natural enzymes, including tyrosinase,[55] hemocyanin[56] and catechol oxidase[57] and a number of other systems have been investigated that show similar types of behaviour and activity to these enzymes.

All of the enzymes mentioned previously possess a (μ-η^2:η^2-peroxo)dicopper(II) (**A**) core at the active site, Scheme 1.23. This bimetallic core is able to reversibly bind O_2 to make use of its oxidising nature in respiration, or in the functionalisation of biochemically important substrates. The **A** type of core has been observed in some synthetic systems,[54] however, for the most part, synthetic systems designed to mimic metalloproteins, have been shown to possess the bis(μ-oxo)dicopper(III) (**B**) core which has two Cu^{3+} metal centres, and in one specific example the facile interconversion between the two cores has been recorded.[53]

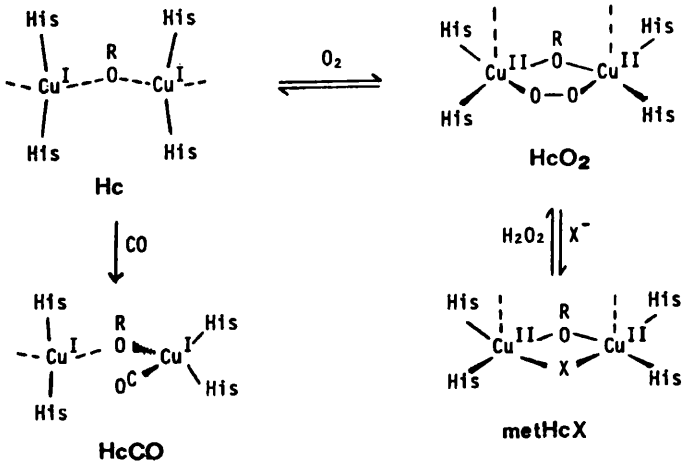
A **B**

Scheme 1.23. Binding modes of O_2 with a dicopper centre.

It has been found that in general tridentate, facially co-ordinating *N*-donor ligands containing bulky substituents, *N*-substituted 1,4,7-triazacyclononane (R_3tacn), tris(pyrazolyl)- and tris(imidazolyl)borates for example, will allow access to the **A** type of core.[53] The **B** core, however, can be stabilised by R_3tacn ligands, containing at least one *N*-alkyl substituent that is not branched.[53]

The dioxygen carrying protein hemocyanin (Hc) is found in molluscs and arthropods and its active centre contains two Cu(I) atoms that are bound by the imidazole groups of three histidine residues. This metal centre is able to form a dioxygen adduct (HcO_2), which is characterised by an electron transfer from the two Cu(I) atoms to the co-ordinated O_2, increasing the metals oxidation state to +2 and decreasing the bond order of O_2 from that in free dioxygen to that in a peroxide. Further reduction of the co-ordinated peroxide would lead to the breaking of the O-O bond, which, although inhibited in dioxygen carrier

enzymes, is fundamental to metalloenzyme catalysed oxidations. Binding of dioxygen to Hc to form HcO_2 is accompanied by a colour change from colourless to blue. The structures of these two forms are relatively well defined, although there is some ambiguity in the precise binding mode of the dioxygen and the geometry about the metal centre. Scheme 1.24 outlines the proposed binding modes for Hc and HcO_2.[58] Oxygen bound to Hc can be displaced by several small molecules including CO, to form HcCO and small nucleophiles (for example N_3^-, NO_2^-, and OAc^-), to form methemocyanins, metHcX.



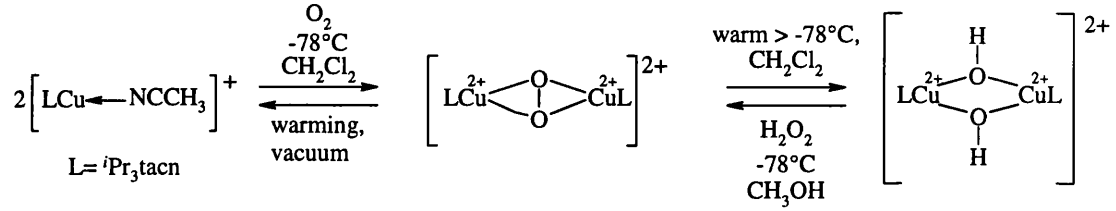
Scheme 1.24. Proposed binding modes of hemocyanin derivatives (dashed lines indicate an uncertainty in the copper's co-ordination number).[58]

The binuclear copper species synthesised by Reed *et al* used a substituted, sterically hindered imidazole ligand arrangement to model the active site of the hemocyanin enzyme.[58] These investigations were more concerned with the structural characterisation of metHcX (X = OAc^-, $HCOO^-$, N_3^-, NO_2^-, and pyrazolate) analogues rather than HcO_2 itself and the complexes so formed were diamagnetic and had an approximately tetragonal stereochemistry with a copper-copper separation of *ca.* 3.6 nm.

Instead of mimicking enzyme centres directly, studies have also been carried out using a variety of *N*-donor ligands, in combination with Cu and other metals, to create other systems that are capable of di-oxygen binding and activation. The ligand 1,4,7-

triazacyclononane, H_3tacn, has featured prominently in such studies.[53] Steric bulk can be easily introduced into this compound, if required, by attaching substituents to some or all of the nitrogens. In addition one or more of the N-H groups can be converted into a substituent that is suitable for attachment to a polymer support.

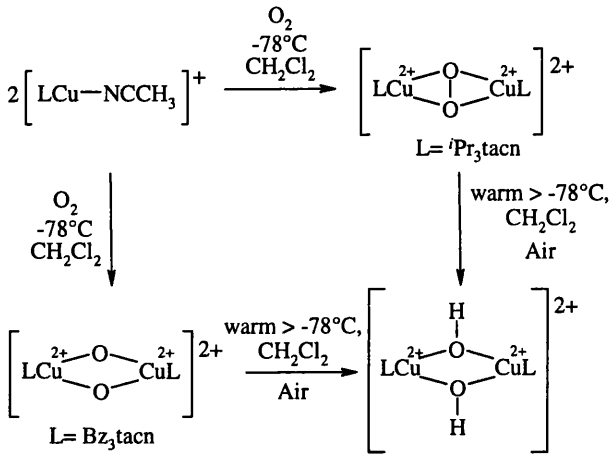
Studies on the $[LCu(NCMe)]^+$ complex (where L = 1,4,7-tri-isopropyl-1,4,7-triazacyclononane, ^{i}Pr$_3$tacn) have shown it to be capable of temperature dependant, reversible di-oxygen binding.[59] The dioxygen adduct is formed by bubbling O_2 through a CH_2Cl_2 solution of the Cu(I) complex at -78°C and it is stable at this temperature *in vacuo* or under a nitrogen atmosphere. When a CH_2Cl_2 solution of the dioxygen adduct is warmed above -78°C, the complex dissociates to its original components. The bridging O_2 was shown, by UV-VIS (λ_{max} = 365 nm), resonance Raman spectroscopy ($\nu_{O\text{-}O}$ =722 cm^{-1}) as well as the complex's EPR silence, to be present as a peroxo species. On exposure to the atmosphere and warming above -78°C, CH_2Cl_2 solutions of this adduct will convert to the hydroxy-bridged derivative Scheme 1.25.



Scheme 1.25. Formation of an A type Cu core.

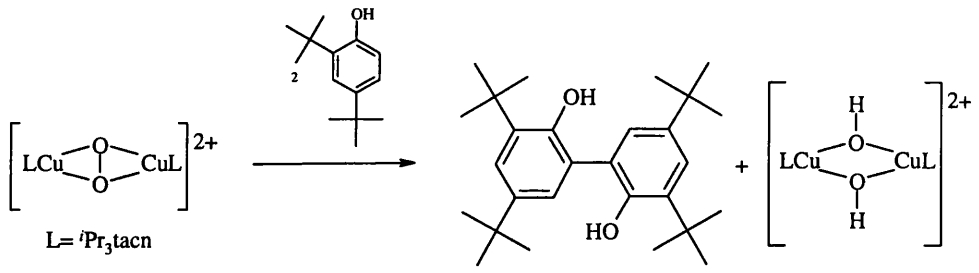
By changing the substituent on R_3tacn it is possible to get both **A** and **B** type of copper cores. If R = benzyl, instead of ^{i}Pr, it was found the **B** bis-(μ-oxo) core was formed, Scheme 1.26.[60] This was demonstrated by UV-VIS (λ_{max} = 318 nm) and resonance Raman spectroscopy ($\nu_{Cu\text{-}O}$ = 602 and 608 cm^{-1}) which showed distinct differences to those found for the ^{i}Pr derivative but remains EPR silent. The benzyl derivative (L = Bz$_3$tacn) otherwise behaves as its ^{i}Pr substituted analogue in that it is thermally unstable and on warming under aerobic conditions, decomposes to give the hydroxy bridged species as shown in Scheme 1.25. It was also noted that on extraction of the copper ions from the hydroxy bridged species, using aqueous NH_4OH, both benzaldehyde and the dealkylation

product Bz_2Htacn were observed, indicating that the ligand was oxidatively attacked on decomposition of the metal complex.



Scheme 1.26. Effect of changing the R substituent of R_3tacn.

The (μ-η^2:η^2-peroxo)copper(II) systems are also implicated in C-H bond activation.[59,61] For example, the dioxygen adduct described previously (Scheme 1.25) has been shown to promote the intramolecular C-C bond coupling reaction of 4,6-di-*tert*-butylphenol *via* the oxidation of an aromatic C-H bond by the Cu_2O_2 unit, Scheme 1.27. During the course of this reaction the Cu_2O_2 core is reduced to the bridging di-hydroxy compound which can then can be re-oxidised back to the μ-η^2:η^2-peroxo species, as shown in Scheme 1.25.

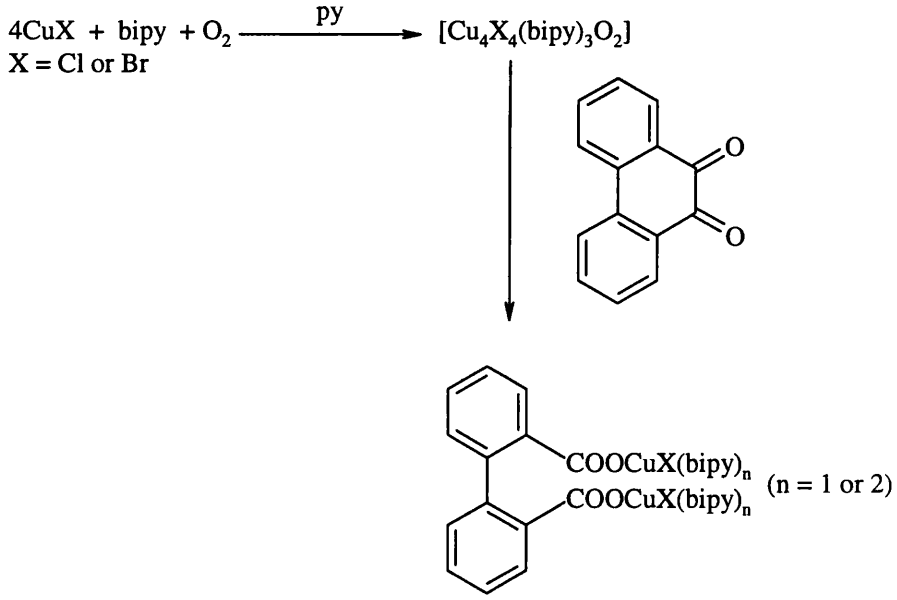


Scheme 1.27. Activation of O_2 to promote C-C bond formation.

The activation of aliphatic carbon-hydrogen bonds could prove useful in the conversion of mustard gas into a less toxic, or harmless, derivative. Alternatively sulfoxidation of HD by such reagents provides another possible route for its destruction, as the S-centre will be easily oxidised.

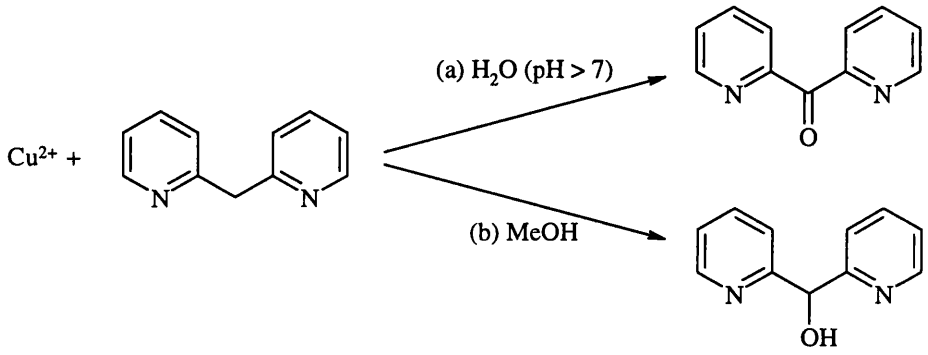
One of the major problems in the development of the chemistry of these types of complex is that, unless formed as intermediates, they are not usually thermally stable, and often decompose to an inactive hydroxy compound at ambient temperatures. As a consequence only a few such complexes have been isolated and fully characterised to date by X-ray crystallography, and their applications outside of the laboratory are limited. Therefore other metal-ligand systems also need to be considered for their oxidising, or O_2 activating, ability.

It was shown that the adduct $[CuCl(py)_2]$ in the presence of O_2 will form an oxo-bridged Cu(II) species.[62] Subsequent investigations showed that similar species can be formed by a variety of ligands containing a pyridyl moiety or other *N*-donor functionality and that they can be used to perform oxidation reactions. For example 9,10-phenanthroquinone was oxidised by O_2 to the corresponding di-acid using CuX (X = Cl or Br) in the presence of either pyridine or 2,2-bipyridine (bipy).[63] By reacting the Cu(I) salt with an excess of bipy and O_2, the $[Cu_4X_4(bipy)_3O_2]$ species initially formed can perform the oxidation shown in Scheme 1.28. The product is easily converted to the free acid, so reforming the $[CuXL_n]$ species.



Scheme 1.28. Oxidation of 9,10-phenanthroquinone by CuX-pyridyl systems.

An alternative to using O_2 to oxidise organic substrates directly is to use redox active metals as the oxidants. These are reduced during the reaction and can be reoxidised by ambient O_2. In the presence of an oxygen atmosphere the copper(I) adduct $[Cu(DPM)]^+$ (DPM = 2,2'-dipyridylmethane) is easily oxidised to the corresponding Cu(II) complex $[Cu(DPM)]^{2+}$.[64] However, in the presence of catalytic amounts of Cu(II) ions in aqueous alkaline media, the central methylene group of the free ligand is oxidised, in the presence of air, to the corresponding ketone (2,2,-dipyridylketone, DPK), Scheme 1.29(a). It has also been shown that in methanolic solutions a similar reaction occurs and that the hydroxylated compound, 2,2'-dipyridylmethanol (DPMOH), is formed, as shown in Scheme 1.29(b).[65] Mechanistic studies show that the role of O_2 in these reactions is to reoxidise Cu(I) to Cu(II) rather than act as a direct oxidant for the organic substrate.



Scheme 1.29. Oxidation of DPM by Cu^{2+} to DPK (a) and DPMOH (b).

The formation of metal-dioxygen adducts is not limited to copper and other metals found in biological compounds, including iron, manganese and cobalt in combination with other *N*-donor ligands, are also capable of activating O_2.[66] As these metals are not relevant to these studies, they are not considered further.

1.3 Method of Delivery of the Catalytic Agent

As catalytic destruction of agents in general, and sulfoxidation of HD in particular, are of interest to this investigation, a method for effective delivery of the catalytic agent to a surface that might be exposed to HD or other agents is required. A support system is required that will allow the catalyst to perform quickly and selectively, but will itself be

inert, non-toxic and non-corrosive. There are two main methods of using catalysts, homogeneously and heterogeneously and both have advantages and disadvantages.

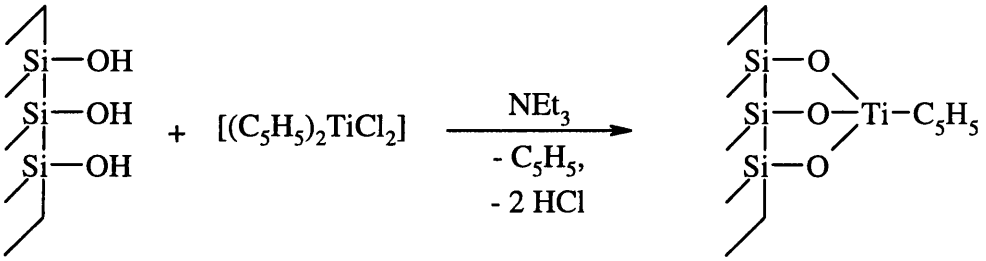
Homogeneous catalysts act in the same phase as the reactants, and usually have a high, solvent-dependant activity and can be used under relatively mild conditions. Other features of this type of catalysis are high selectivity and specificity with easily defined and interpreted activity. Mechanistic information can often be elucidated without too much ambiguity, so offering the possibility of modifying and controlling activity in a systematic way. There are serious problems associated with homogeneous systems though. The separation of the catalyst from the reaction mixture can sometimes prove difficult or impossible. Some catalytic systems are very unstable, needing carefully controlled conditions for storage and use, they are also sensitive to "poisons" which deactivate them.

In comparison heterogeneous catalysts perform in a different phase to the reactants and are more robust. The catalyst can be easily separated from the reactants and products, and heterogeneous catalysts are often stable enough to be used at high temperature and pressures with a variety of solvents. Although they have a high activity, heterogeneous catalysts have a limited usefulness in the range of reactions that can be carried out, and they often lack specificity and selectivity. The mechanisms involved can be complex, involving adsorption, desorption, and interaction with the support, making the identification of reactive intermediates very difficult.

A comparison of the characteristics of homo- and heterogeneous catalysts shows that a beneficial point of one is frequently a problem with the other. A combination of the good aspects without any of the bad ones would be very advantageous. Being able to combine the activity of homogeneous catalysts, with the ease of separation of heterogeneous catalysts, led in recent decades to the development of "heterogenised-homogeneous," or "supported," catalysts. By immobilising ligating species on a polymeric backbone, or other solid supports, molecular sieves for example,[67] followed by subsequent metallation, heterogenised-homogeneous catalysts can be produced and evaluated.

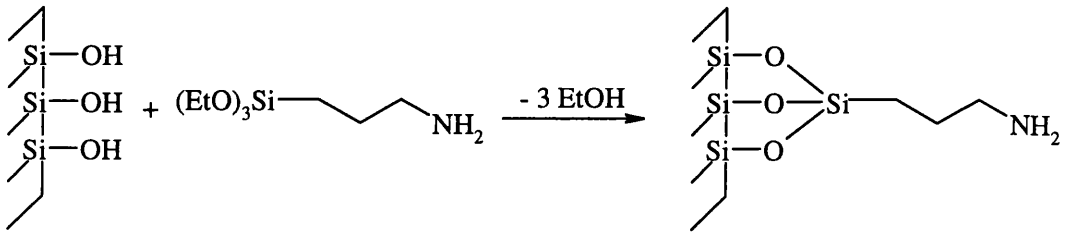
1.3.1 Heterogenised-Homogeneous Catalysts

Metal complexes that are able to catalyse particular reactions can be attached to a support by various methods, which depend critically on the nature of the support material. These methods include direct grafting of the metal to a silica surface utilising the terminal silanol bonds, Scheme 1.30.[68]



Scheme 1.30. The grafting of Ti to a silica surface.

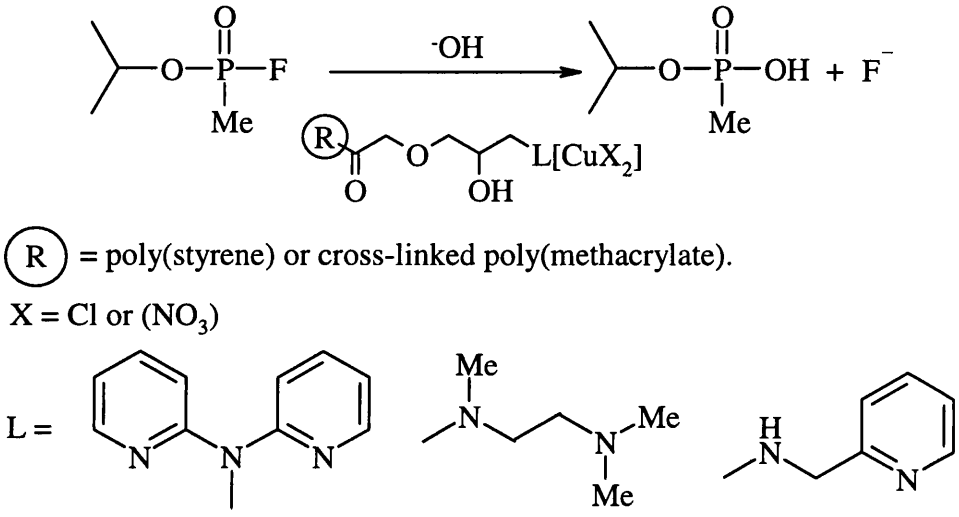
A second method involves the prior attachment of a ligand to a solid support, silica for example, which is then able to complex with an active metal centre, Scheme 1.31.[69]



Scheme 1.31. Attaching a potential ligand to a silica surface.

By making the supporting material a solid, as is often the case, separation of the products of the reaction from the catalyst becomes easier, whilst the presence of the metal centres on the surface mimics the characteristic well-defined catalytic activity of analogous homogeneous systems. It is necessary to establish in these cases that dissociation of the metal species from the ligand does not occur if the system is to be considered truly heterogeneous.

Blacker *et al.* very recently used this approach by supporting metallated ligands on organic polymers for studying the catalytic hydrolysis of the nerve agent Sarin.[70] A range of bidentate *N*-donor ligands were supported on both linear styrene polymers and cross-linked methacrylate resins, and subsequently metallated with $CuCl_2$ and $Cu(NO_3)_2$, Scheme 1.32. It was found that these supported catalysts were far less active than the unsupported analogues, but the ease of separation of the supported catalysts from the reaction solution and their recycling were positive advantages. Another advantage of this type of system is that the catalyst can be immobilised on the polymer at a specific concentration; this allows a certain degree of control over reaction rates.

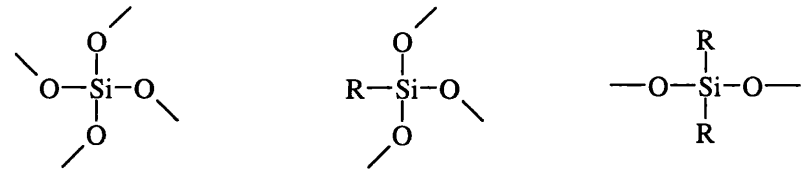


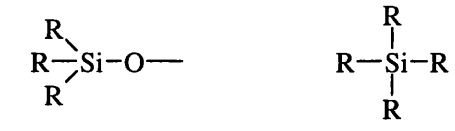
Scheme 1.32. Hydrolysis of Sarin using $[LCu(NO_3)_2]$ based catalysts.

Unlike homogeneous catalysts, supported catalysts may not have all active sites available for catalytic transformations, and the catalytic activity of certain metal complexes will change when supported on the polymer. In addition most organic polymers are not stable at elevated temperatures. This can lead to degradation of the support under forcing conditions so rendering the catalyst useless. The effect of swelling of some polymers, caused by a solvent, can alter diffusion rates and also change the catalytic activity. The use of inorganic polymers, organosiloxanes in particular, is a potential area of interest. Organosiloxanes are thermally more robust than most organic polymers, are non-toxic, easily handled, resistant to a wide variety of chemicals as well as being lipophilic (as is HD) and highly permeable to gases, including O_2. Organosiloxanes can also be used as coatings, cast as films, or as fluids.

1.3.2 Organosiloxanes

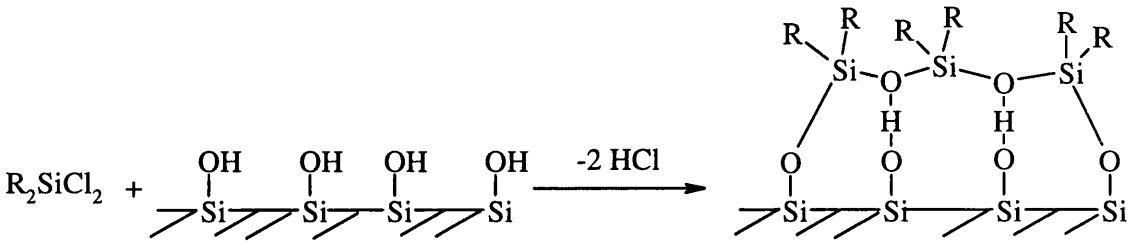
Siloxanes consist of repeating Si-O sub-units, and are derived from SiR_4 (where R = H or other alkyl or aryl substituent) in which one or more R groups are replaced by a Si-O linkage, Scheme 1.33. Pure silica exists as a network polymer made up of SiO_4 tetrahedra, and it has an inflexible three-dimensional structure with silanol, Si-OH, units covering the surface of the solid. As organic groups replace the oxygens of the SiO_4 units the nature of the structure also changes. The unit $RSiO_3$, containing a single organic group, retains the three dimensional network structure, but now the silicon has been "capped" by a non-bridging hydrophobic substituent. Diorganosiloxanes, of the general formula $(R_2SiO)_n$ will form linear polymers (poly(dimethylsiloxane), PDMS, where R = Me) or cyclic species (for example hexamethylcyclotrisiloxane, $Me_6Si_3O_3$, where n = 3). The R_3SiO unit is only able to dimerise.[71] The different electronic environment around each type of silicon in organosiloxanes is reflected in their different ^{29}Si NMR chemical shifts. For example the R_3SiO unit gives rise to a ^{29}Si resonance in the range of $\delta \sim 0 - 40$ ppm, whilst the R_2SiO_2 moiety gives a signal in the range $\delta \sim -50 - 0$ and the $RSiO_3$ unit appears in the range $\delta \sim -125 - -50$ ppm.[72] These chemical shift values are all dependent on the nature of the substituent R.





Scheme 1.33. The different stoichiometries of organosiloxane fragments in relation to a tetraorganosilane.

Organosilicon monomers, particularly R_2SiCl_2, are the basis of commercial "silicones" and have a wide variety of other uses. They are frequently utilised as hydrophobic agents for the treatment of inorganic surfaces, glass and silica for example. The monomeric dialkyldihalosilanes react directly with surface hydroxyl groups, and are also easily hydrolysed on surfaces to form water repellent siloxane oligomers, Scheme 1.34.



R = alkyl or aryl

Scheme 1.34. Functionalisation of a silica surface with a diorganodihalosiloxane.

The polymeric diorganosiloxane species are of interest in this investigation, the reasons for this are discussed in more detail in **Section 1.3.3** below.

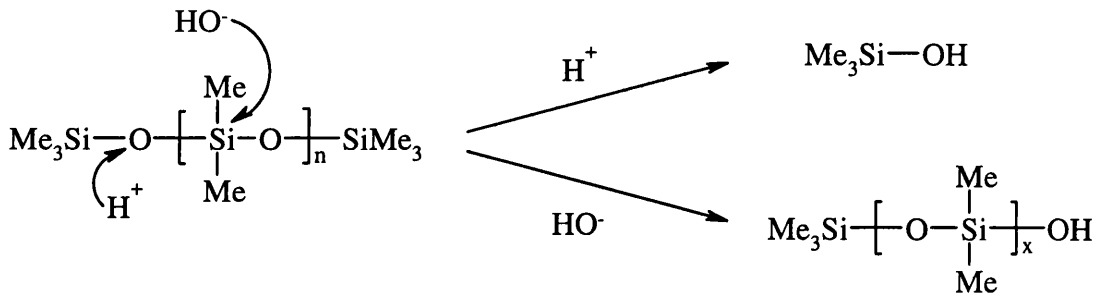
1.3.3 Poly(organosiloxanes)

Unfunctionalised linear poly(dimethylsiloxanes) exist as stable, non-toxic fluids. Other fluid siloxane derivatives, such as the commercially available hydride $Me_3SiO(MeSi(H)O)_nSiMe_3$ (n = *ca.* 35) are easily functionalised *via* hydrosilylation or dehydrocoupling reactions, to afford linear functionalised siloxanes which, unlike organic polymers of similar molecular weight, are generally mobile fluids. The addition to the polymer of low concentrations of side-arm functionalities consisting of a spacer chain terminated by a ligating group does not generally reduce their fluidity greatly, and thus the resultant products can be used as solvents and as fluid catalyst supports in some organic reactions.

The backbone of all siloxane polymers is made up of Si-O repeat units, which have a high thermal and chemical stability. The Si-O-Si bond has a bond energy in the region of 420-490 kJ mol^{-1},[71] and it is also very flexible. This bond angle can vary from between

109-180° without any significant loss of bond strength. In addition to these features the Si-R (R = aliphatic) rotational bond energy is much less than that for the corresponding C-R linkage. The flexibility of the polymer backbone and the low intermolecular forces between polymer chains, means that they can be easily extended or deformed by applied forces; they have relatively high compressibilities for example, and their dielectric constant varies very little with temperature. The gas permeability of poly(organosiloxanes) is very high (permeability of O_2 in PDMS = *ca.* 4550 Barrers), and most poly(organosiloxanes) have good chemical stablilities as well as ozone and UV resistance.

Poly(organosiloxanes) are susceptible to both electrophilic and nucleophilic attack, usually by strong acids or bases, Scheme 1.35. However, the polar Si-O backbone is protected by the organic substituents, thus minimising scission under anything but fairly extreme conditions.

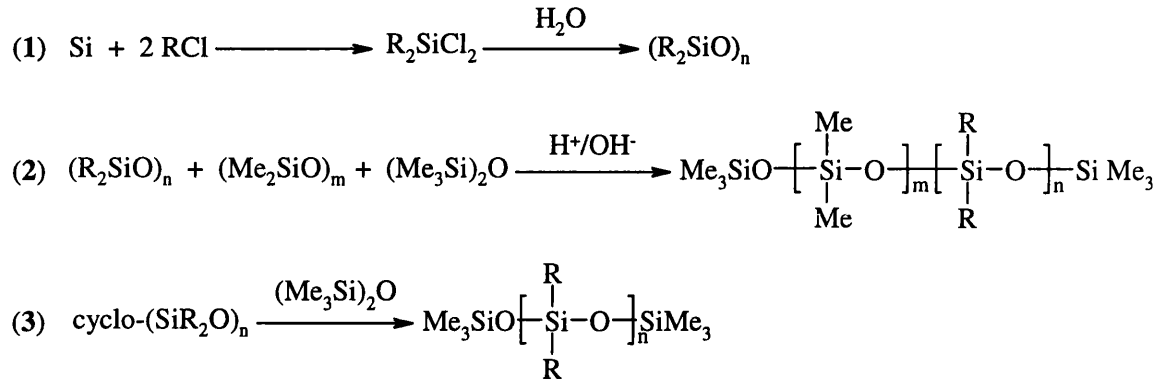


Scheme 1.35. Initial reaction between PDMS and an acid or base.

1.3.4 Functionalised Poly(organosiloxanes)

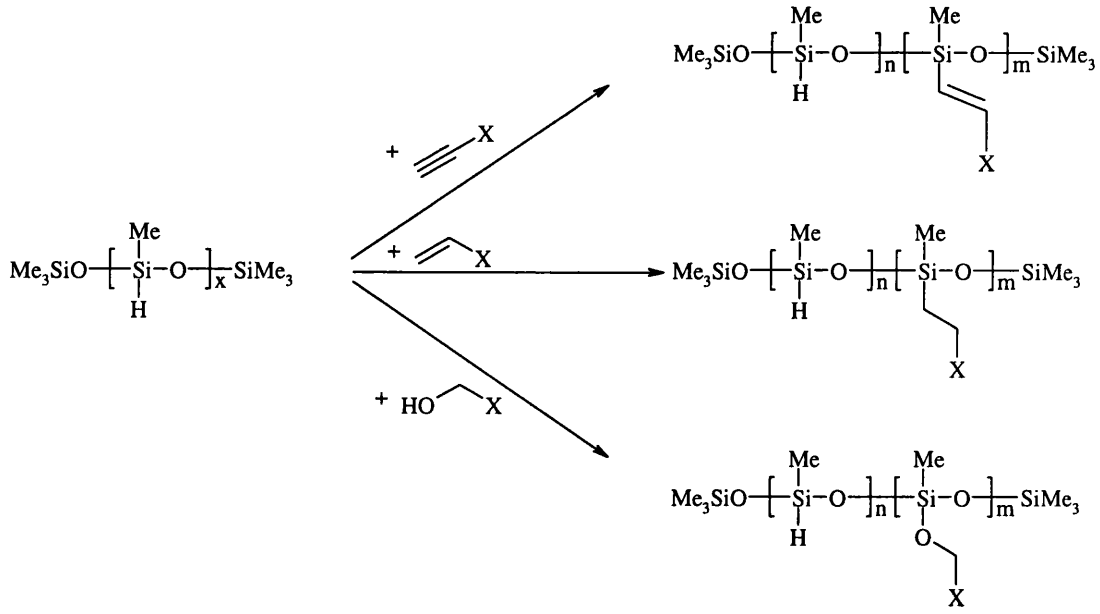
The synthesis of functionalised linear poly(organosiloxanes) can be achieved *via* one of a number of methods as outlined in Scheme 1.36. Two of the methods are similar but arise from different precursors. The first involves the preparation of a dichlorodiorganosilane, R_2SiCl_2 (where R is an organic functionality), which can be synthesised by reacting silicon with a suitable alkyl halide. This can be hydrolysed to form organofunctional siloxane oligomers, which in turn can be polymerised. Cyclic siloxanes are also formed in the hydrolysis of dichlorodiorganosilanes, and can undergo anionic ring-opening polymerisation to yield poly(organosiloxanes). The second method is to perform a co-

polymerisation of a silanol functionalised organosiloxane, with a dimethylcyclosiloxane and a chain-terminating agent, with an acid or base as the catalyst.



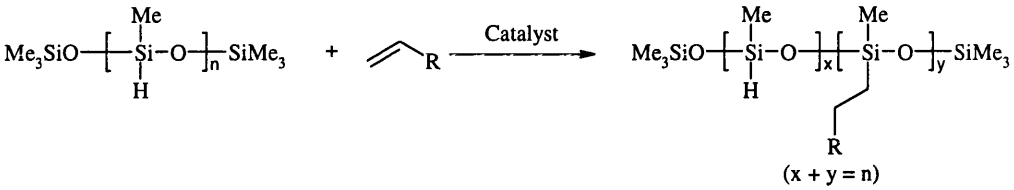
Scheme 1.36. Synthetic methods of functionalising poly(siloxanes).

The siloxanes formed by either reaction can be further functionalised if one or more of the R substituents is a reactive group such as a hydride. The Si-H units can react with other organic residues containing a terminal -OH group (dehydrocoupling) or an unsaturated functionality (hydrosilylation), alkenes or alkynes for example Scheme 1.37. These methods are discussed in more detail in **Sections 1.3.4.1** and **1.3.4.2** below.



Scheme 1.37. Hydrosilylation and dehydrocoupling reactions.

When a hydrosilylation reaction is performed with the polymeric species, poly(methylhydrosiloxane), PMHS in excess, only some of the Si-H units react to form organic substituents. The degree of substitution is known as the "percentage loading" and can be anywhere from 0 (unfunctionalised polymer with all Si-H units intact) to 100% (completely substituted polymer with no Si-H units left), Scheme 1.38.



Scheme 1.38. Hydrosilylation of a linear poly(siloxane) with an indeterminate loading of substituent.

The actual number of additions to the polymeric backbone can only be controlled to some degree by the stoichiometry. Steric hindrance, especially at higher loadings, often affects the final stoichiometry. However loadings of the organofunctionalised polymer can be conveniently determined from ^{1}H NMR data. By comparing the integrals of the Si-H, Si-Me and Si-R resonances it is possible to determine the actual loading of the substituent on the polymer.

1.3.4.1 Hydrosilylation

Hydrosilylation is the preferred method in this investigation for introducing a range of different side-arm functionalities into a poly(siloxane). The Si-C-C linkage that is formed when an alkene adds to a silane is considerably more stable both thermally and hydrolytically than the Si-O-C linkage formed from the dehydrocoupling reaction of an alcohol with a silane (see **Section 1.3.4.2**). Organofunctionalised silanes are normally formed using one of two synthetic methodologies; radical initiated, and metal catalysed, hydrosilylation. The choice of method depends on the substrate as well as the degree of specificity desired. Each method is discussed in more detail below.

1.3.4.1.1 Radical Initiated Hydrosilyations

Radicals generated by UV or γ-radiation, AIBN, or peroxides can be used to effect hydrosilylation reactions.[73] The mechanism involves in each case initiation, propagation and chain termination steps. The radicals generated attack the Si-H bond of the silane causing homolytic cleavage and so producing a silyl radical. This radical then reacts with the olefin to create a Si-C-C linkage, also as a radical species, which reacts with a second silane molecule abstracting the proton from that and creating the non-radical hydrosilylation product. Also produced in this step is another silane radical which perpetuates the chain reaction. Investigations into this mechanism have shown that the silyl radicals will only react with only the CH_2 group of the olefin thus resulting in the *anti*-Markownikoff addition product.[74] This process is illustrated in Figure 1.6 below.

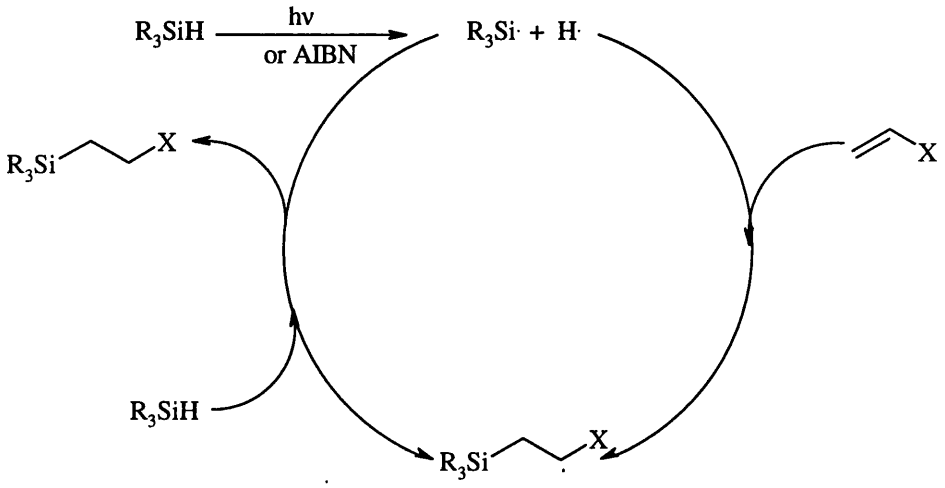


Figure 1.6. Radically initiated hydrosilylation reaction.

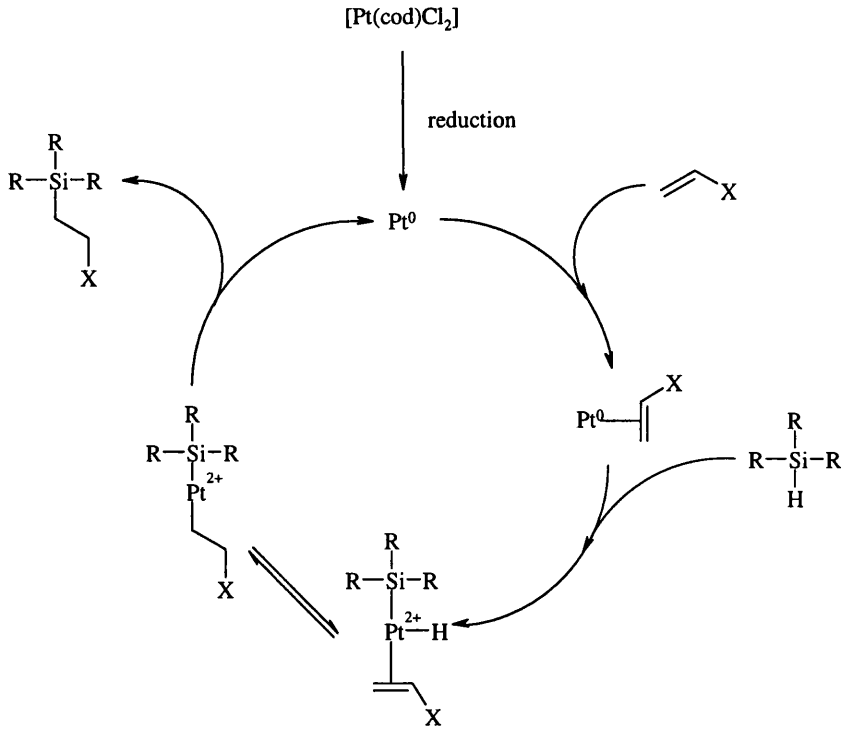
Some olefins undergo radically initiated polymerisation as a side reaction, and not all solvents are suitable for use. All reactants and solvents have to be deoxygenated to prevent the formation of singlet oxygen, which is a powerful oxidising agent and will produce oxidation side products such as diols and silanols.

1.3.4.1.2 Metal Catalysed Hydrosilylations

The metal catalysts commonly used for hydrosilylation are platinum[75,76] or rhodium[77] based, but aluminium,[78] lanthanide[79] and titanocene[80] based catalysts have also been investigated. Platinum catalysts show high catalytic activity and the mechanism of this reaction has also been thoroughly investigated for this metal. Various Pt based catalysts are commonly used in hydrosilylation reactions, including hexachloroplatinic acid, $H_2PtCl_6 \cdot xH_2O$ (also known as the Spiers' catalyst), platinum(1,5-cyclooctadiene) dichloride, [Pt(cod)Cl_2], and platinum(0) tetravinyldimethyldisiloxane, (also known as the Karstedt catalyst).

It was originally suggested by Chalk and Harrod that the platinum catalysed reaction was typical of many other catalytic cycles in that three steps could be used to describe it: oxidative addition, ligand combination and reductive elimination.[75] Further work in this area carried out by Lewis and Lewis using [Pt(cod)Cl_2] confirmed these suggestions but it was also found that colloidal platinum(0) is the active catalytic species.[81]

Lewis and Lewis reported that a slow initial induction step takes place, in which the Pt(IV) or Pt(II) compound undergoes reduction by Si-H species to Pt(0). Once this has been formed an alkene can co-ordinate to the metal centre to form an alkene complex with no change in the formal oxidation state of the metal. The Si-H unit of the silane then oxidatively adds to the Pt(0), by *trans*-metallation, thus forming a Pt(II)-hydride complex. The hydride and the alkene can then combine to form a discrete metal-alkyl species before a reductive elimination step combines the two fragments to form the substituted silane or siloxane and regenerates the Pt(0) catalyst. Both Markownikoff and *anti*-Markownikoff addition are possible, but in general the less sterically hindered product is greatly favoured. The mechanism that was proposed is shown in Scheme 1.39.



Scheme 1.39. Proposed mechanism for the hydrosilylation reaction using [Pt(cod)Cl_2] as catalyst.

The order of reactivity of Pt based catalysts is generally Pt(0)>Pt(II)>Pt(IV). This is due in part to the Pt(II) and Pt(IV) species having to first form colloidal Pt(0), and partly due to these having lower solubilities in typical hydrosilylation solvents. Catalysts of the type Pt(0)L_x, where L is an olefin, are particularly effective. The Karstedt catalyst, which has in the solid state two Pt(0) centres linked by three tetravinyldimethyldisiloxanes, is miscible with siloxanes and is particularly valuable and effective in this area of chemistry.

1.3.4.2 Dehydrocoupling

By reacting a linear siloxane, containing one or more hydrides, with a suitable alcohol it is possible to create a Si-O-C linkage. This reaction is normally Zn or Sn catalysed but it can also be catalysed using a Pt catalyst as for hydrosilylation. The presence of a catalyst is not vital as the reaction can proceed uncatalysed, but this is a much slower process.

The mechanisms for the catalysed reaction are shown in Figure 1.7(a) below. Mechanistic studies of this reaction suggest that the metal catalyst initially activates the H-Si bond.[82]

For most metal catalysts this occurs either through oxidative addition (Route 1) or *via* the formation of a σ-complex (Route 2). In either route, attack of the alcohol on the silicon atom results in dissociation of the product from the metal, *via* molecular hydrogen formation. A third pathway is exhibited by Sn(IV) catalysts, Figure 1.7(b)

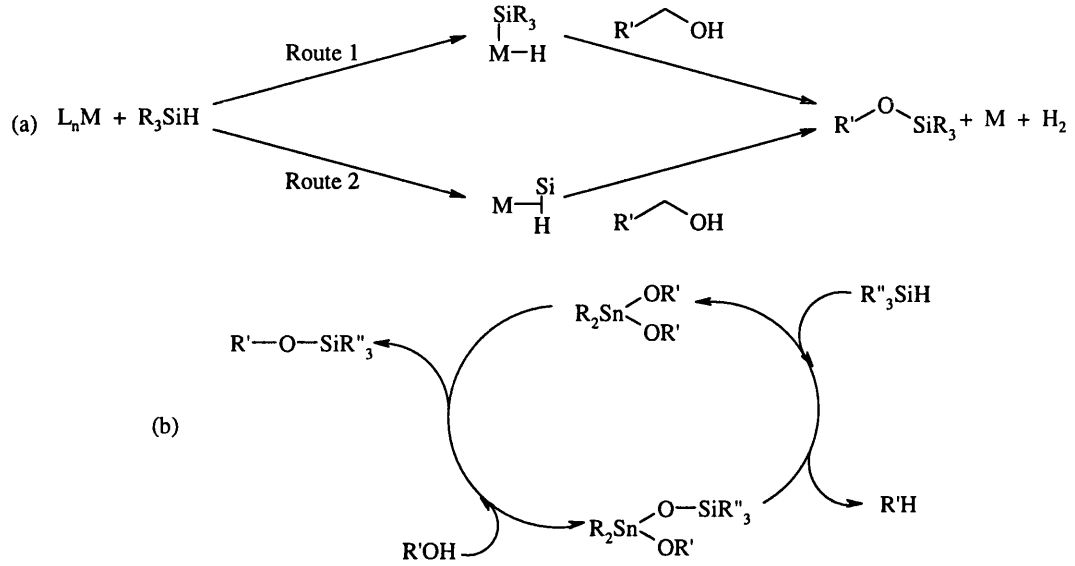
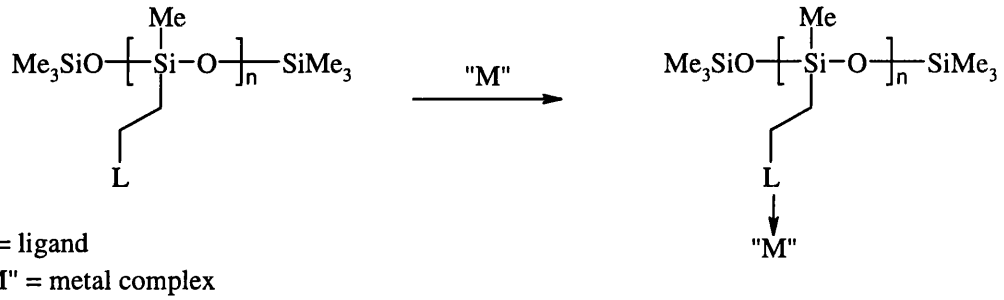


Figure 1.7. Mechanisms for dehydrocoupling.

This method is useful for introducing different organic moieties into the siloxane but there are problems associated with both the reaction itself and the stability of the product. In the dehydrocoupling product the Si-O bond has a higher bond energy (*ca.* 450 $kJmol^{-1}$) than the C-O bond (*ca.* 360 $kJmol^{-1}$),[83] and oxygen is more electronegative than either silicon or carbon, (which have electronegativities of *ca.* 1.8 and 2.5. on the Allred and Rochov scale, respectively). This means that cleavage at the Si-O-C linkage is likely to occur at the C-O bond under acidic conditions, and at the Si-O bond under basic conditions. In addition the dehydrogenation of two Si-H units to form new Si-O-Si linkages rather than Si-O-C linkages can occur. This results in cross-linking and traces of water facilitate this process. If the alcohol used for dehydrocoupling contains a terminal alkene moiety, *O*-silylation in most cases is greatly preferred over *C*-silylation.[76(iii)]

1.3.5 Metallation of Linear Organofunctionalised Siloxanes

If a linear organosiloxane has been functionalised with a suitable ligating species, it can then be metallated, thus producing a supported metallic species. Metallation is normally achieved by reacting the siloxane with a metal complex in a solvent that is compatible with both components, Scheme 1.40. Complete or partial metallation may be controlled through stoichiometry.



L = ligand
"M" = metal complex

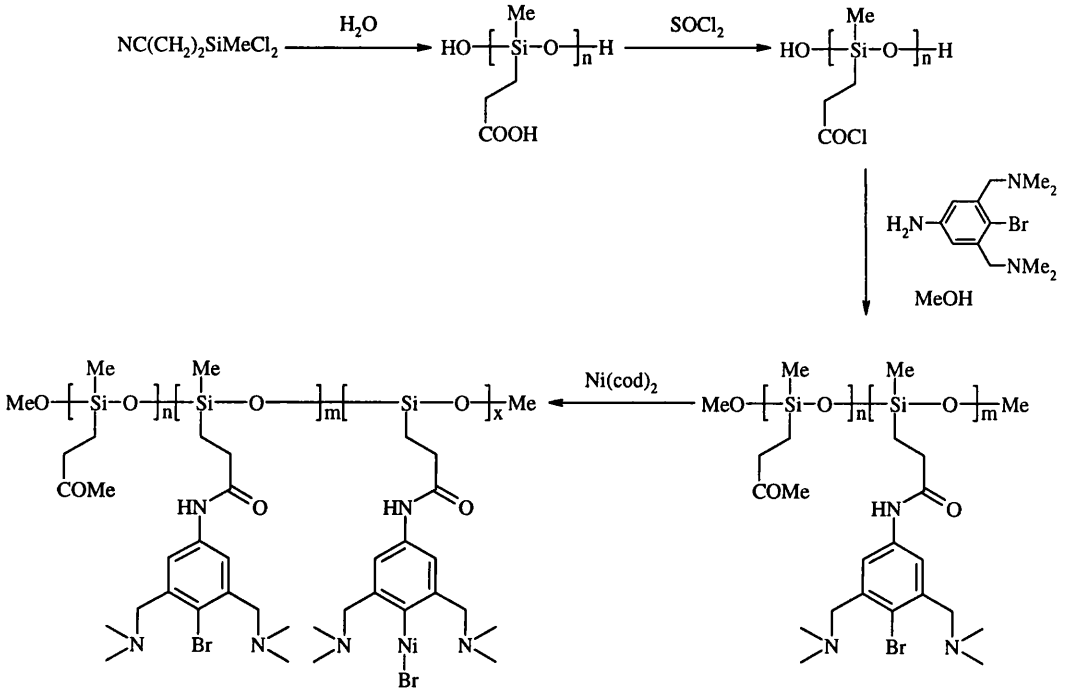
Scheme 1.40. Metallation of a ligand functionalised siloxane.

As linear ligand-functionalised poly(diorganosiloxanes) are rarely crystalline, and even after metallation remain as fluids or amorphous solids, their characterisation relies heavily on spectroscopic techniques. X-ray crystallography can be utilised to determine the co-ordination geometry around the metal-free ligand centre, but it has then to be assumed that the metal will be in a similar environment when reacted under similar conditions with the organofunctionalised siloxane containing the same ligand terminus.

Although the range of functionalities that can be attached to siloxanes has potentially no limit, relatively few ligand-containing siloxanes and their corresponding metallated derivatives have been reported, for either oligo- or poly(siloxanes). Ligand terminated siloxanes of interest in the context of this study include phosphines, alkenes, amines, cyano and pyridyl ligands.[84,85,86] Several of these have been reacted with various metal salts, including those of rhodium, molybdenum, iron and nickel.[85,86]

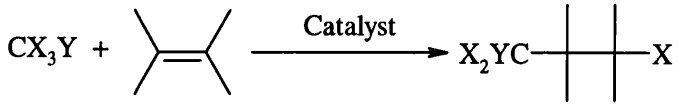
In very few instances ligand functionalised poly(siloxanes) have also been synthesised by modification of side-arm substituents. In one such report, methyldichloro(3-cyanopropyl)silane was initially polymerised by hydrolysis, so affording the carboxylic

acid functionalised poly(siloxane).[86] This was then converted to the acyl chloride before being reacted with a primary aromatic amine containing two tertiary amine groups capable of co-ordinating to metals, Scheme 1.41.



Scheme 1.41. Synthesis of a polymer bound Ni catalyst.

On metallation with $[Ni(cod)_2]$ a polymer supported catalyst for the Kharasch addition of polyhalogenated alkanes to alkenes (Scheme 1.42) was formed. The catalytic activity of this supported catalyst was found to be higher than for the corresponding unsupported metal catalysts.

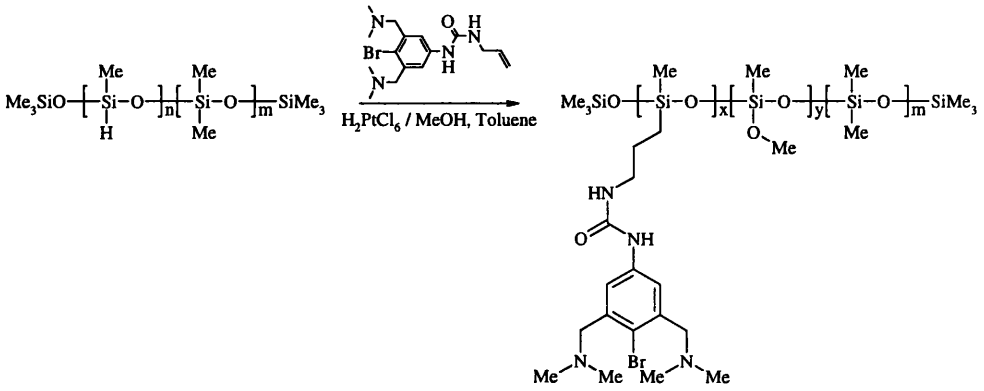


X = halogen,
Y = H, halogen, CF_3 or other electron withdrawing group.

Scheme 1.42. The Kharasch addition of polyhalogenated alkanes to alkenes.

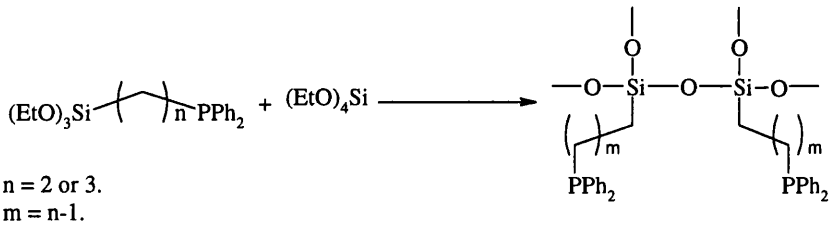
It was also shown that a similar polymer could be prepared using hydrosilylation between the alkenyl functionalised ligand and a poly(methylhydro-dimethylsiloxane). Methanol

was used to cap any unreacted hydrides, Scheme 1.43, but no metallation experiments were reported on these materials.[86]



Scheme 1.43. Synthesis of polymer bound ligating species *via* hydrosilylation.

A related methodology for the synthesis of siloxane supported co-ordination compounds was used by Parish *et al.*[87] An insoluble, solid poly(siloxane) ligand was first formed from the hydrolytic condensation of $[(Et_2O)_3Si(CH_2)_nPPh_2]$ with $Si(OEt)_4$, Scheme 1.44. On treatment of this solid with the complex $[IrCl(cod)]_2$ it was found that, although not all of the tertiary phosphine groups were complexed, the species formed showed significant activity for catalytic hydrogenations.

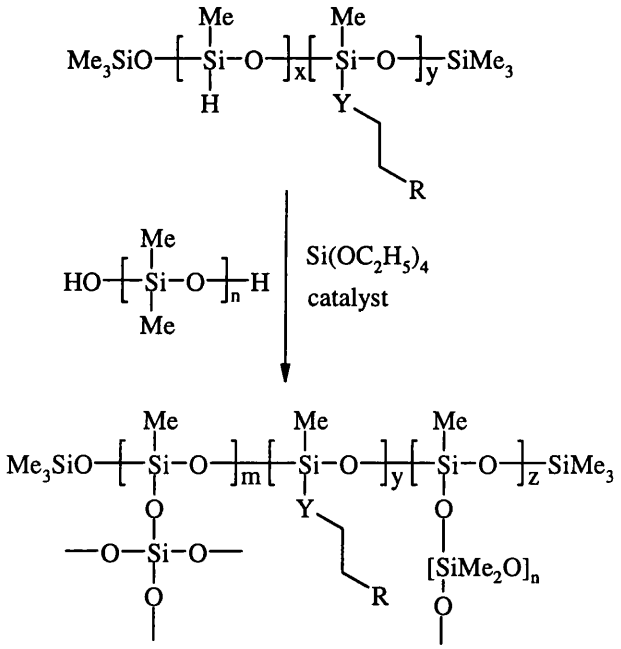


Scheme 1.44. Preparation of a phosphinated siloxane.

These and earlier reactions reveal the potential of siloxane-supported metal systems in catalysis.[36-38]

1.3.6 Membrane Formation

Once a linear poly(organosiloxane) has been suitably functionalised the polymers can be cross-linked and pressed into a thin film. This can be readily accomplished using remaining Si-H units in the linear polymer to cross-link with an α,ω-disilanol-poly(dimethylsiloxane). By using a relatively low molecular weight polymer as a cross-linking agent, a high percentage loading of functional groups in the membrane can result. Traces of tetraethoxysilane are also usually added during the cross-linking process, to finally remove any remaining unreacted silanol or Si-H groups at the end of the cross-linking process. A metal catalyst, typically a Pt(II) or Sn(IV) compound, is added to speed up the cross-linking. The film can be cast, or more normally pressed, to produce a membrane *ca.* 50-100 microns thick. Heating to 80-100°C for several days eliminates all traces of volatile materials, thus "curing" the membrane. This type of poly(organosiloxane) membrane retains the high oxygen permeability of the linear material, and such films have been used as films to mediate the growth of inorganic solids,[88] in gas separation,[89] and in pervaporation.[90]



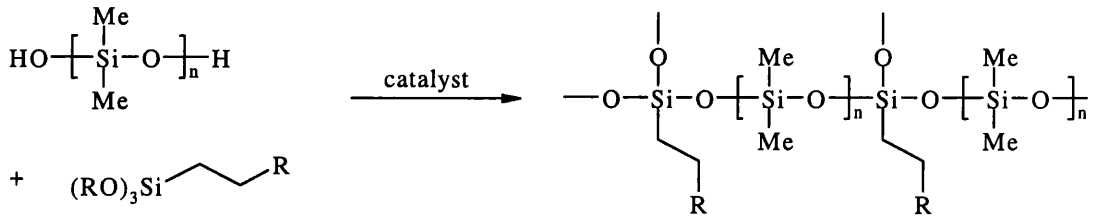
Scheme 1.45. Crosslinking of a functionalised poly(siloxane) into a membrane.

The degree of substitution of the linear poly(siloxane) will have an effect on the characteristics of the membrane. At low loadings there is generally a random distribution

of substituents, but as the degree of substitution is increased a block co-polymer type pattern becomes evident in those materials examined so far.[88] There is potential therefore for producing membranes in which some areas are hydrophobic and others are hydrophilic. Being able to predetermine these domains would be very useful, but has not yet been achieved.

The side chains will also have an effect on the nature of the membrane produced. Fluorinated alkyl chains, for example, impart increased water repellence so producing an oleophobic membrane. Nucleophilic compounds attached to the polymeric backbone have the potential to react with other compounds that come in contact with the membrane. If a ligand is attached to the polymer it can easily be metallated and thus produce an active, organo-poly(siloxane) supported, catalyst system. On cross-linking the poly(siloxane), the polymer supported catalyst has in effect been turned into a membrane supported catalyst, with the permeability of the membrane controlling the rate of reaction.

Certain functionalities do not lend themselves to hydrosilylation reactions. Olefins containing sulfur for example will poison most catalysts, so an alternative method must be used to introduce them into a membrane. By using an organofunctional trialkoxysilane to cross-link a silanol terminated poly(dimethylsiloxane), a membrane can be created directly, Scheme 1.46. A wide variety of organic groups can be accommodated, provided they can be synthesised or are commercially available. With this method it is possible to produce a high loading of the functionality in the membrane. Addition of small quantities of PMHS to increase the degree of cross-linking is also a known modification of this method.



Scheme 1.46. Membrane formation from a functionalised trialkoxysilane.

1.4 Summary

The research carried out in this programme was designed to develop methodologies for producing siloxane supported catalysts and reagents suitable for the safe and efficient decontamination of chemical warfare agents, in particular, but not exclusively, mustard gas. The decontaminant must be deliverable in a form suitable for application to a variety of different situations, for example coatings for different types of surface, which might be contaminated with chemical agents.

For the purposes of this investigation organosiloxanes are of interest because of the following features:

- They can be functionalised with a wide variety of organic groups including potential ligating species, which can then be metallated at the molecular level.
- A combination of functional groups can be added by sequential reactions.
- They can be cross-linked to produce surface coatings.
- They form highly oxygen permeable films and coatings.
- Solid species can be dispersed into the fluid polymers or cross-linked films, which could either act as absorbents or as heterogeneous decontamination catalysts
- Key properties (such as hydrophobic/hydrophilic balance) can be controlled by the choice and degree of functionalisation.

It is for these reasons that it was proposed that model, short-chain siloxanes and poly(organosiloxanes) should be functionalised with suitably modified ligating species. These organofunctionalised materials would be metallated with selected metal species that show catalytic activity towards either hydrolysis or the activation of molecular oxygen. Routes to cross-linked siloxane membranes containing the above, as well as films containing finely divided reactive solids incorporated directly within them, were also of interest in this programme.

Complexes formed between Cu(II) and bi- or tri-dentate *N*-donors have been shown previously to be excellent hydrolysis catalysts for organophosphates.[70] It has also been shown that Cu(II) with bi- or tri-dentate *N*-donor ligands are known to be potential

oxidants, either by "activating" O_2[53-63] or performing the oxidation themselves and being aerobically re-oxidised from Cu(I) to Cu(II).[64] Therefore, it was proposed that these investigations would centre on systems containing *N*-donor ligands and their Cu(II) derivatives. Zn(II) salts have been shown to be good hydrolysis catalysts[91] and are suitable for NMR studies to aid in structural identification. Consequently a few zinc analogues were also prepared.

Structural studies aimed at elucidating any differences between M-(*N*-ligand) and M-(*N*-alkenylated-ligand) analogues were an important feature in these studies

Materials of interest for the destructive oxidation of HD or hydrolysis of organophosphate based chemical agents, were to be made available for testing elsewhere by the project sponsors (DERA).

1.5 Programme of Research

The results of this investigation are split into four sections, each of which will be described in subsequent chapters.

- **Chapter 2** details the synthesis and characterisation of acyclic *N*-donor ligands and their modifications, as well as their attachment to a siloxane framework, and reactive membrane formation.
- **Chapter 3** describes analogous investigations using cyclic *N*-donor ligands.
- **Chapter 4** is concerned with the preparation and characterisation of the adducts formed between the free ligands and Cu and Zn salts.
- **Chapter 5** describes future directions for this area of research.

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Chapter 2:

Acyclic *N*-Donor Ligands and Poly(siloxane) Membranes Containing Dispersed Solids

Chapter 2: Acyclic *N*-Donor Ligands and Poly(siloxane) Membranes Containing Dispersed Solids.

2.0 Introduction 57

2.1 Acyclic *N*-Donor Ligands 57

2.1.1 2,2'-Dipyridylamine, Hdpa 57

2.1.1.1 2,2'-Dipyridyl(*N*-propenyl)amine, Prdpa, 1 59

2.1.1.2 2,2'-Dipyridyl(*N*-pentenyl)amine, Pedpa, 2 60

2.1.2 Bis-(2-methylpyridyl)amine, Hbmpa, 3 62

2.1.2.1 Bis-(2-pyridylmethyl)(*N*-propenyl)amine, Prbmpa, 4 65

2.1.3 2-Methylamino(*N*-methyl-*N*-2-hydroxyethyl)pyridine, Mamp, 5 67

2.2 Organofunctionalised Siloxanes 70

2.2.1 Introduction 70

2.2.2 Reactions of Acyclic *N*-Donor Ligands with Hmts 70

2.2.2.1 Prdpa 70

2.2.2.2 Pedpa 72

2.2.2.3 Prbmpa 74

2.2.2.4 Mamp 74

2.2.3 End Group Manipulation 75

2.3 Membranes Containing Dispersed Solids. 76

2.3.1 Carbon and Silica Containing Membranes (11-16) 77

2.3.2 Copper(II) and Zn(II) Hydroxide Containing Membranes (17-23) 78

2.4 Conclusions 80

2.5 References. 81

2.0 Introduction

During these investigations a range of acyclic and cyclic nitrogen donor ligands were synthesised and then metallated. As noted in **Chapter 1**, *N*-donor ligands are widely used in metal complexes that are oxidation and hydrolysis catalysts, or activate O_2 for use as an oxidising agent. This chapter first describes the investigations into the synthesis of appropriately modified acyclic ligands. The spectral and analytical characterisation of each of the compounds is given in detail in the **Experimental** (**Chapter 6**). **Note:** The NMR data presented in **Chapters 2-4** (**Figures 2.3**, **2.4**, **2.6-2.8**, **3.1**, **3.3** and **3.5**) were all recorded at a field strength of 270 MHz, whilst **Figure 4.13** was recorded at 400 MHz.

2.1 Acyclic *N*-Donor Ligands

In **Section 1.3.4** two of the more widely used methodologies for organofunctionalising poly(siloxanes) were discussed. These involve the reaction between either a 1-alkenyl- or a hydroxyl-terminated organic residue. with one or more of the Si-H units present in the siloxane. Therefore, in order to attach a ligating species to a model or polymeric siloxane using one of these routes, the ligand has to contain a spacer chain terminated by an alkene or hydroxyl group. Acyclic ligands containing one or more pyridyl units are attractive candidates because of their role in a variety of catalytic processes including oxidation and hydrolysis.[1,2]

2.1.1 2,2'-Dipyridylamine, Hdpa

The ligand 2,2'-dipyridylamine, Hdpa, was originally synthesised in 1914 from 2-chloropyridine and 2-aminopyridine,[3] but it is now readily available from commercial sources. In the neutral ligand the central N-atom is not strongly basic, but imparts a degree of flexibility to the ligand.

It has been reported to possess a number of possible co-ordination modes towards metal centres, in both the protonated and deprotonated forms, as shown in Figure 2.1 below.[4,5,6,7]

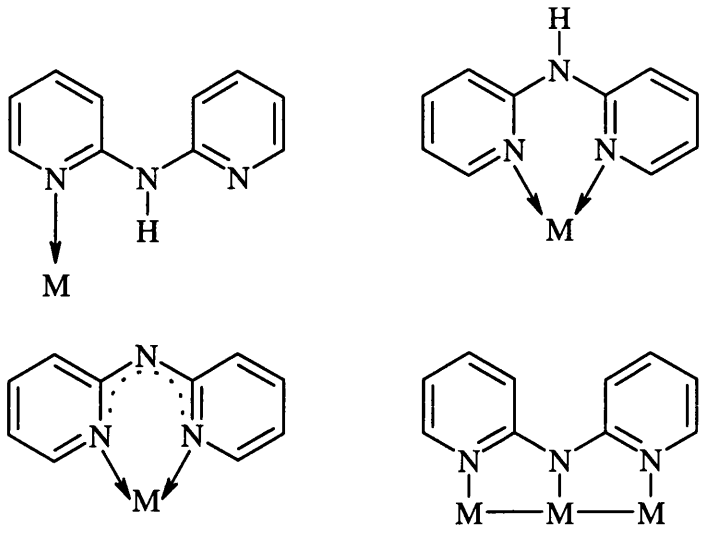
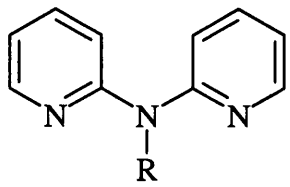


Figure 2.1. Different co-ordination modes of Hdpa and the [dpa]⁻anion.

The secondary amine moiety in Hdpa can also be functionalised with a range of different substituents to afford a series of tertiary amine ligands of general formula Rdpa. Examples include methyl,[8] phenyl,[9] pyridyl,[10] trimethylsilyl,[11] benzyl[12] and hexyl[13] groups, Figure 2.2.



R = Me, Ph, py, TMS, $CH_2C_6H_5$, $CH_3(CH_2)_5$.

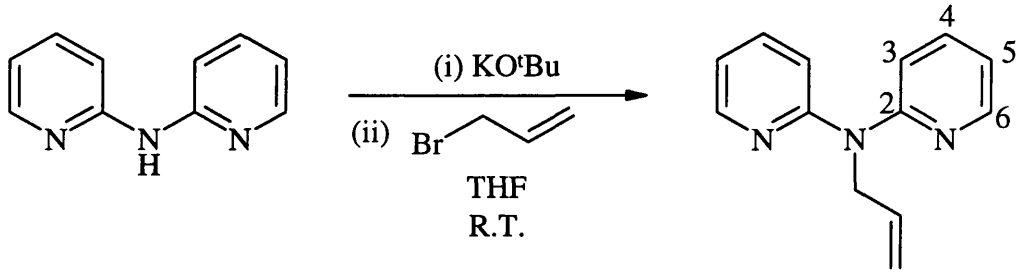
Figure 2.2. *N*-Substituted 2,2'-Dipyridylamine.

In this investigation Hdpa has been functionalised with two different lengths of 1-alkenyl chains in order to make it suitable for attachment to the Si-H moieties of a poly(organosiloxane).

2.1.1.1 2,2'-Dipyridyl(*N*-propenyl)amine, Prdpa, 1

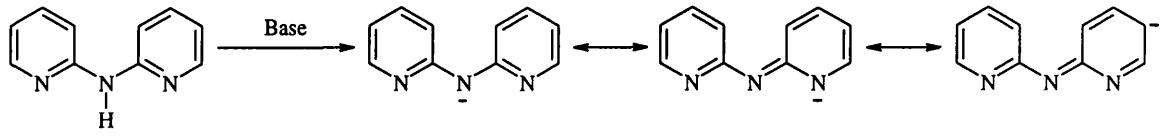
The ligand 2,2'-dipyridyl(*N*-propenyl)amine has been reported previously,[8] and its complex with $CuCl_2$ was synthesised but not characterised. Prdpa was synthesised by Dorokhov *et al* by reacting allyl bromide with Hdpa in MeCN, in the presence of Bu_4NBr, using electrolysis techniques.[8] In these investigations an alternative synthetic methodology was used.

The reaction of Hdpa with allyl bromide in THF, in the presence of KO^{t}Bu, afforded **1,** after purification by column chromatography, as a dark yellow oil, in *ca* 30% yield, Scheme 2.1. It is miscible with most common organic solvents and was characterised using ^{1}H and ^{13}C NMR as well as IR spectroscopy and microanalysis.



Scheme 2.1. Synthesis of 1 and its numbering scheme.

On initial deprotonation of Hdpa by a base the negative charge on the [dpa]$^-$ anion can be delocalised around both aromatic rings, Scheme 2.2. Thus both *N*- and *C*-alkenylation are possible reactions. After **1** had been eluted in the first fraction from the chromatography column, further fractions were collected using the same solvent system, in an attempt to isolate any other products formed, but the only product successfully identified in them was unreacted Hdpa.

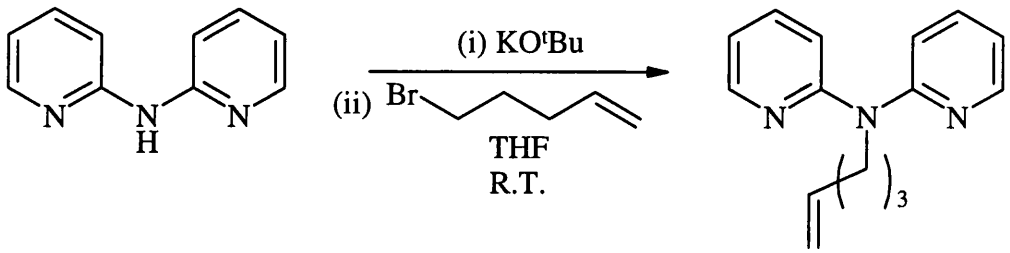


Scheme 2.2. Resonance stabilisation of the [dpa]$^-$ anion.

Data from the ^{1}H NMR (Figure 2.3) and ^{13}C spectra of **1** correlate well with values reported previously.[8] In both the ^{1}H and ^{13}C NMR spectra the chemical shifts assigned to the pyridyl protons and carbons of **1** are in very similar positions to those reported for Hdpa,[13] indicating that the addition of the propenyl chain has no real influence on these atoms. The doublet in the ^{1}H NMR spectrum of **1** at δ = 4.86 ppm, is assigned as the *N*-CH_2 protons of the propenyl chain. These protons have a higher chemical shift than those found in either dioctylallylamine[14] or allyldiphenylamine[15] (δ = 3.07 and δ = 4.36 ppm respectively). This is due to the increased electron withdrawing nature of the pyridine rings in **1**, which deshield the methylene protons of the alkenyl chain more than either saturated alkyl or non-heteroaromatic substituents.

2.1.1.2 2,2'-Dipyridyl(*N*-pentenyl)amine, Pedpa, 2

In order to investigate whether a longer alkenyl chain attached to the exocyclic nitrogen of Hdpa would better facilitate hydrosilylation, the ligand 2,2'-dipyridyl(*N*-pentenyl)amine was synthesised. The synthetic methodology used was identical to that used for **1** but with 5-bromo-1-pentene replacing allyl bromide. The required product was isolated as a dark yellow oil, but in only in very low (11%) yield, Scheme 2.3. Attempts to modify the preparative procedure did not improve the yield. It is possible that the lower reactivity of the C-Br bond of 5-bromo-1-pentene, as compared to that in allyl bromide, accounts for the low yield.



Scheme 2.3. Synthesis of 2.

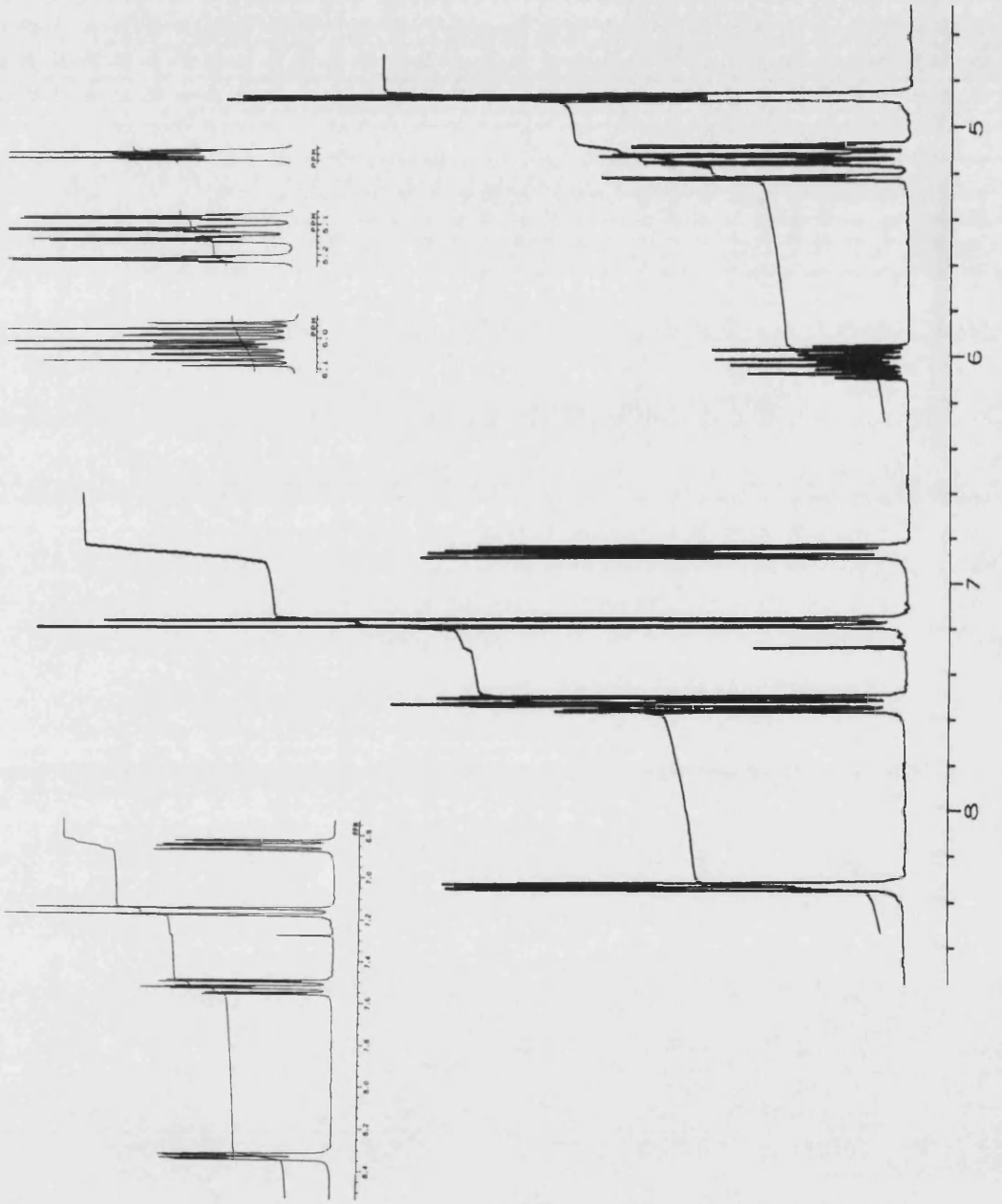


Figure 2.3. ^{1}H NMR spectrum of 1 recorded in $CDCl_3$.

As expected the aromatic region of the ^{1}H NMR spectra of both **1** (Figure 2.3) and **2** (Figure 2.4) were almost identical with respect to proton splitting patterns and chemical shifts. The two sets of doublet of doublets and the doublet of doublet of triplets arising from the -CH=CH$_2$ (see **Experimental**) residue in Pedpa resonate at lower chemical shifts (δ = 491, 4.95 and 5.83 ppm, *cf.* 5.40, 5.42 and 6.02 ppm for **1**). The methylene unit α to the tertiary amine appears as a triplet at δ = 4.20 ppm, compared to the corresponding signal for 2,2'-dipyridyl(*N*-hexyl)amine at δ= 4.15-4.19 ppm.[13] The two remaining methylene units of the pentenyl chain of **2** appear as a quintet at δ = 1.81 ppm and a quartet at δ = 2.12 ppm.

The ^{13}C NMR data for **2** also show close similarities to those of **1**. All five aromatic carbons of the pyridyl rings resonate in the region of δ = 114-157 ppm, and appear within $\pm$ 2.0 ppm of the corresponding signals for **1**. The two unsaturated alkenyl carbons have slightly lower chemical shifts than those in **1,** as they are less deshielded by the pyridyl ring. The methylene carbon α to the exocyclic N atom is more deshielded than in **1,** as it is now well separated from the effect of the terminal alkenyl moiety. The remaining signals, at δ = 27.4 and 31.2 ppm, are assigned to the two remaining methylene groups.

2.1.2 Bis-(2-methylpyridyl)amine, Hbmpa, 3

Bis-(2-methylpyridyl)amine is a tridentate chelating ligand that usually co-ordinates facially to metal centres. The methylene spacer groups between the pyridyl rings and the secondary amine moiety make the ligand less rigid than Hdpa and increase the basicity of the exocyclic N-atom, such that all three nitrogens can co-ordinate to the same metal centre. The secondary amine moiety of **3** has also been functionalised with a range of different substituents to form a series of tri- and tetra-dentate tertiary amine ligands, Rbmpa. Examples include R = methyl (Me),[16] hydroxypropyl,[17] methylpyridyl (picolyl),[18] aminoethyl,[19] benzyl (Bz)[16] and *t*-butyl (^{t}Bu),[20] Figure 2.5.

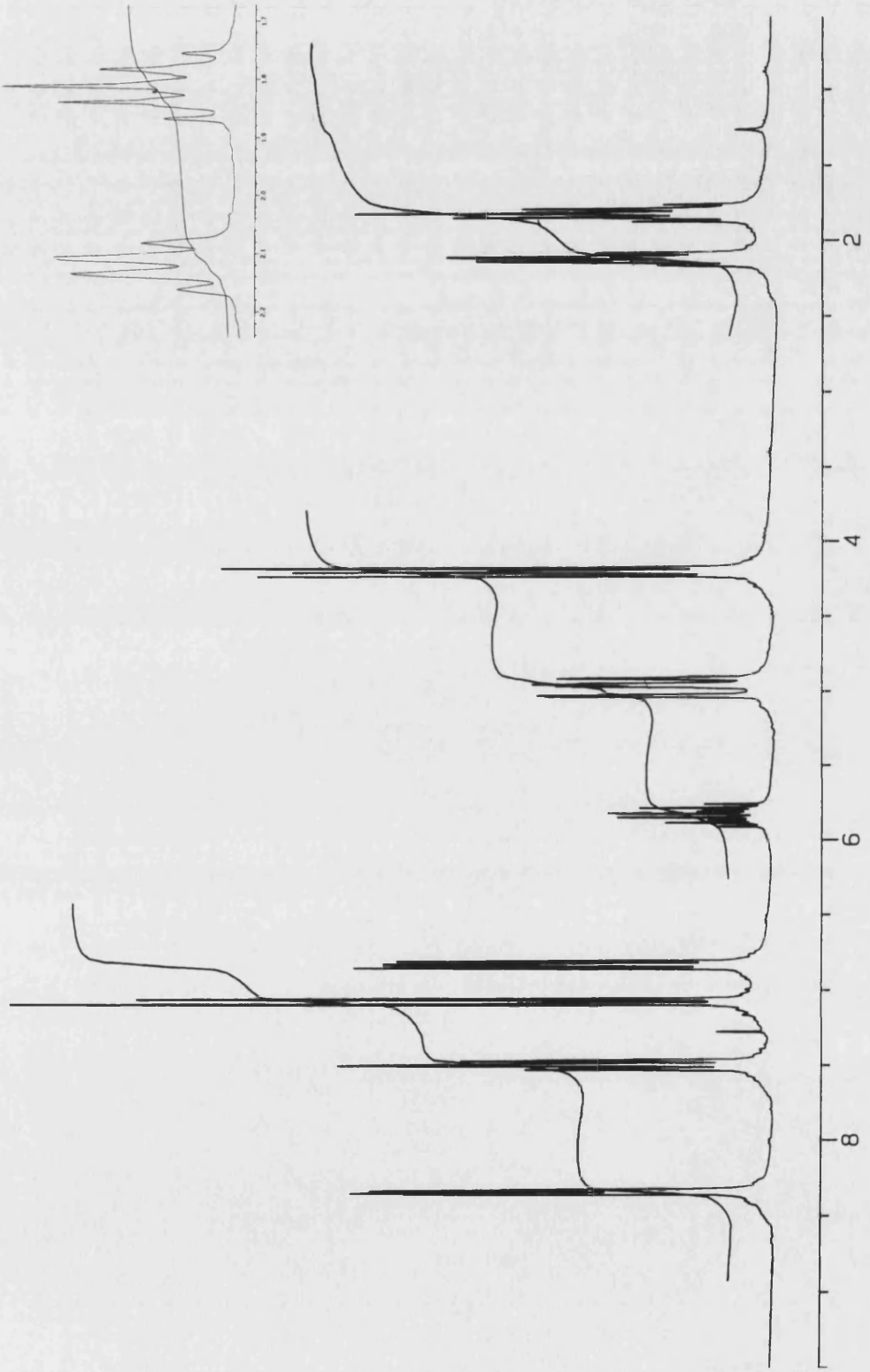
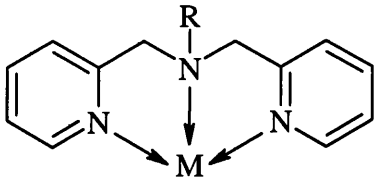


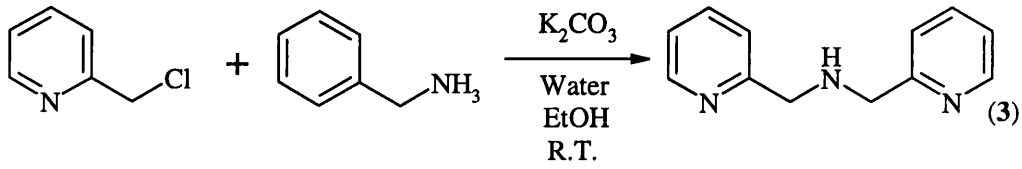
Figure 2.4. ^{1}H NMR spectrum of 2 recorded in $CDCl_3$



R = H; Me; Bz; picolyl; ^{t}Bu; aminoethyl; hydroxypropyl.

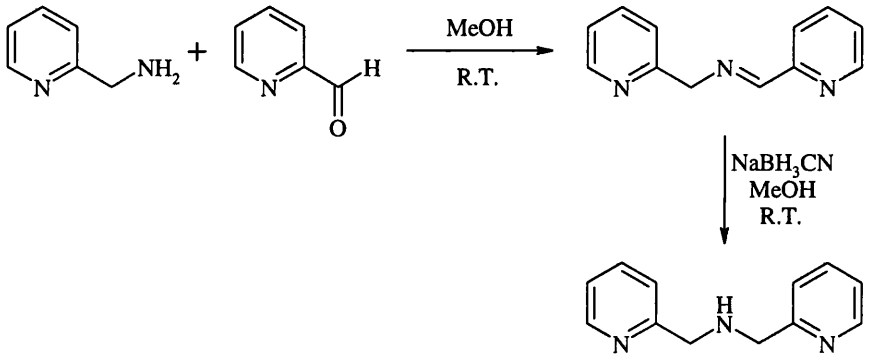
Figure 2.5. Co-ordination mode of Rbmpa.

During this investigation **3** was synthesised using two different literature procedures, as described below, before being functionalised with a 1-alkenyl chain.[21,22] The first method involved the reaction between 2-(chloromethyl)pyridine and 2-(aminomethyl)pyridine, in the presence of K_2CO_3, Scheme 2.4.[21] After purification by Kugelrohr distillation, **3** was isolated as a yellow oil in lower overall yields than reported in the literature (*cf.* 29% compared with 49%[21]).



Scheme 2.4. Synthesis of 3.

The second procedure involved a reductive amination reaction between 2-amino-methylpyridine and 2-pyridinecarboxaldehyde with the initial Schiff base being reduced to the desired product by $Na[BH_3CN]$, Scheme 2.5.[22] The product **3** is formed in high yields (80%) at ambient temperatures, and is also almost 100% pure, following removal of excess reactants and volatiles.

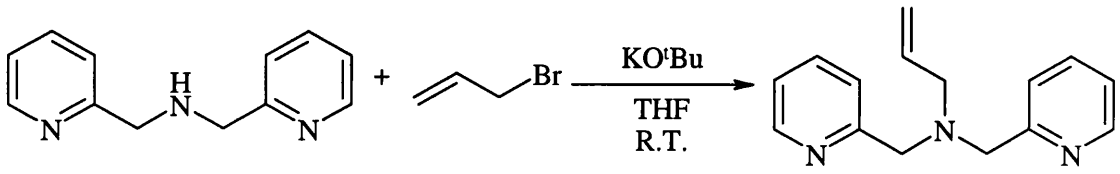


Scheme 2.5. Alternative synthesis of 3.

The ^{1}H (Figure 2.6) and ^{13}C NMR data for **3** have been reported previously and the data found in this study for **3** produced using either synthetic methodology, were in good agreement, and are not commented on further.[23]

2.1.2.1 Bis-(2-pyridylmethyl)(*N*-propenyl)amine, Prbmpa, 4

Compound **3** was *N*-alkenylated in an analogous manner to that used for Hdpa, and **4** was isolated, after purification by flash chromatography, in moderate yields, as a brown oil that is miscible with most common organic solvents, Scheme 2.6.



Scheme 2.6. Synthesis of 4.

The pattern of resonances in the aromatic region of the ^{1}H NMR spectrum of **4** (Figure 2.7) is very similar to that of its precursor **3**. For both the *N*-butyl and *N*-benzyl analogues of **4**, *n*-Bubmpa and Bzbmpa respectively,[24] three of the pyridyl ring protons have δ = 7.00-7.66 ppm, with the fourth appearing at δ = 8.57 ppm in the former and δ = 8.48 ppm in the latter. Thus the substituent R has little effect on the aromatic protons in any of these derivatives. However the chemical shift of the methylene protons in the spacer group between the pyridyl rings and the central amine moiety changes by almost 0.2 ppm on both *N*-alkylation and *N*-alkenylation.[24]

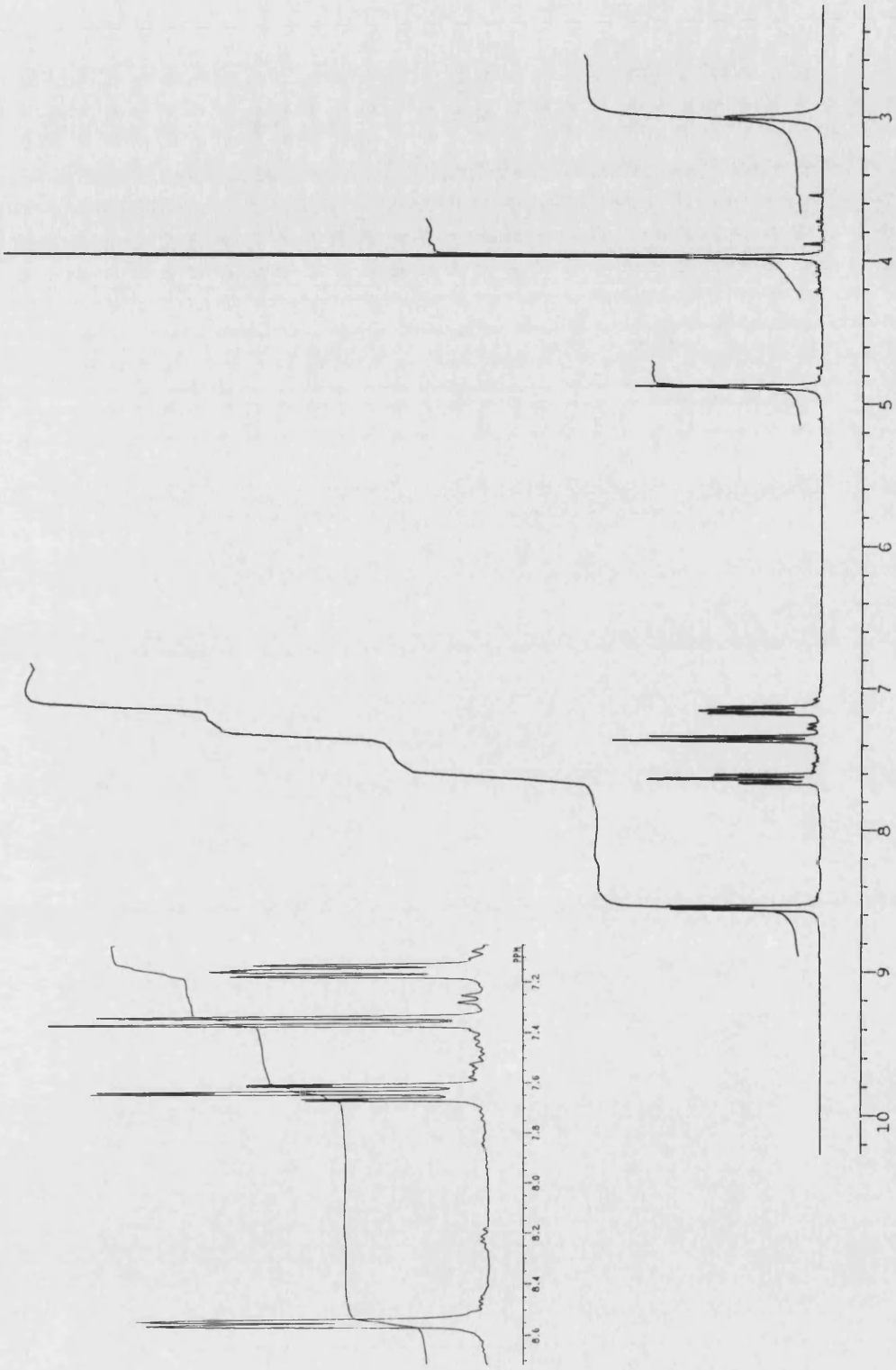


Figure 2.6. ^{1}H NMR spectrum of 3 recorded in $CDCl_3$.

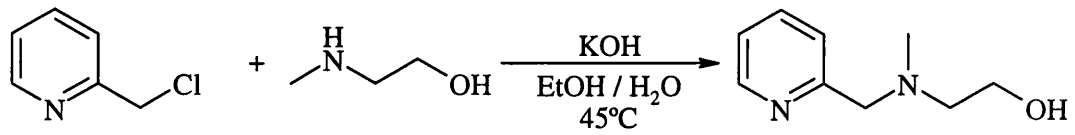
Comparisons between the ^{13}C NMR spectra of 3 and 4 reveal only small differences in the aromatic region. The chemical shift of the methylene spacer units between the pyridyl rings and the central amine change slightly ($\delta = 54.5$ ppm in **3**, 60.0 ppm in **4** and 60.4 ppm for Bzbmpa).[24] Significantly the carbon signals associated with the propenyl chain in 4 have substantially different chemical shifts from those in **1**. Thus the methylene groups between the electron-withdrawing pyridine rings and the exocyclic *N*-atom in **4** "insulate" the *N*-alkenyl substituent from the electronic effects of the aromatic rings.

A brief attempt was also made to synthesise the pentenyl homologue of **4** using the same methodology but none of the desired product was isolated.

2.1.3 2-Methylamino(N-methyl-N-2-hydroxyethyl)pyridine, Mamp, 5

As described in **Section 1.3.4.2**, an alternative method for adding an organic functionality to a Si-H unit in a siloxane involves a reaction with a terminal alcohol. One such acyclic compound containing this functionality, together with a pyridyl unit attached to the exocyclic amine, was prepared for attachment to a model trisiloxane.

By reacting the free base of 2-(chloromethyl)pyridine hydrochloride with *N*-methyl-aminoethanol in aqueous ethanol, **5** was obtained as a yellow oil in moderate yields (57 %), Figure 2.8. Both the ^{1}H NMR (Figure 2.8) and ^{13}C NMR spectra of **5** agree with the data previously reported.[25] Although this is a known compound its reactivity towards metal ions has yet to be explored.



Scheme 2.7. Synthesis of 5.

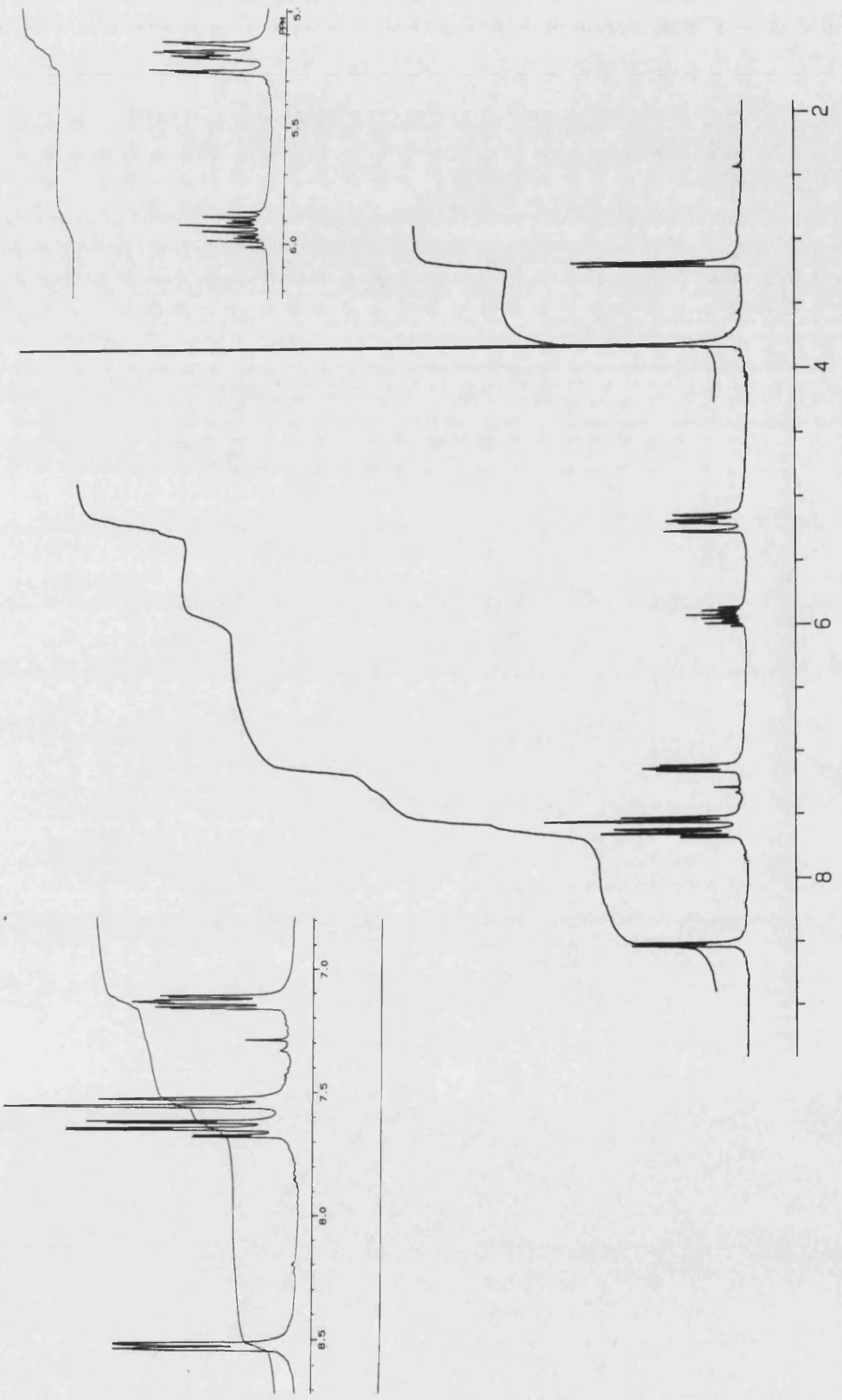


Figure 2.7. ^{1}H NMR spectrum of 4 recorded in $CDCl_3$.

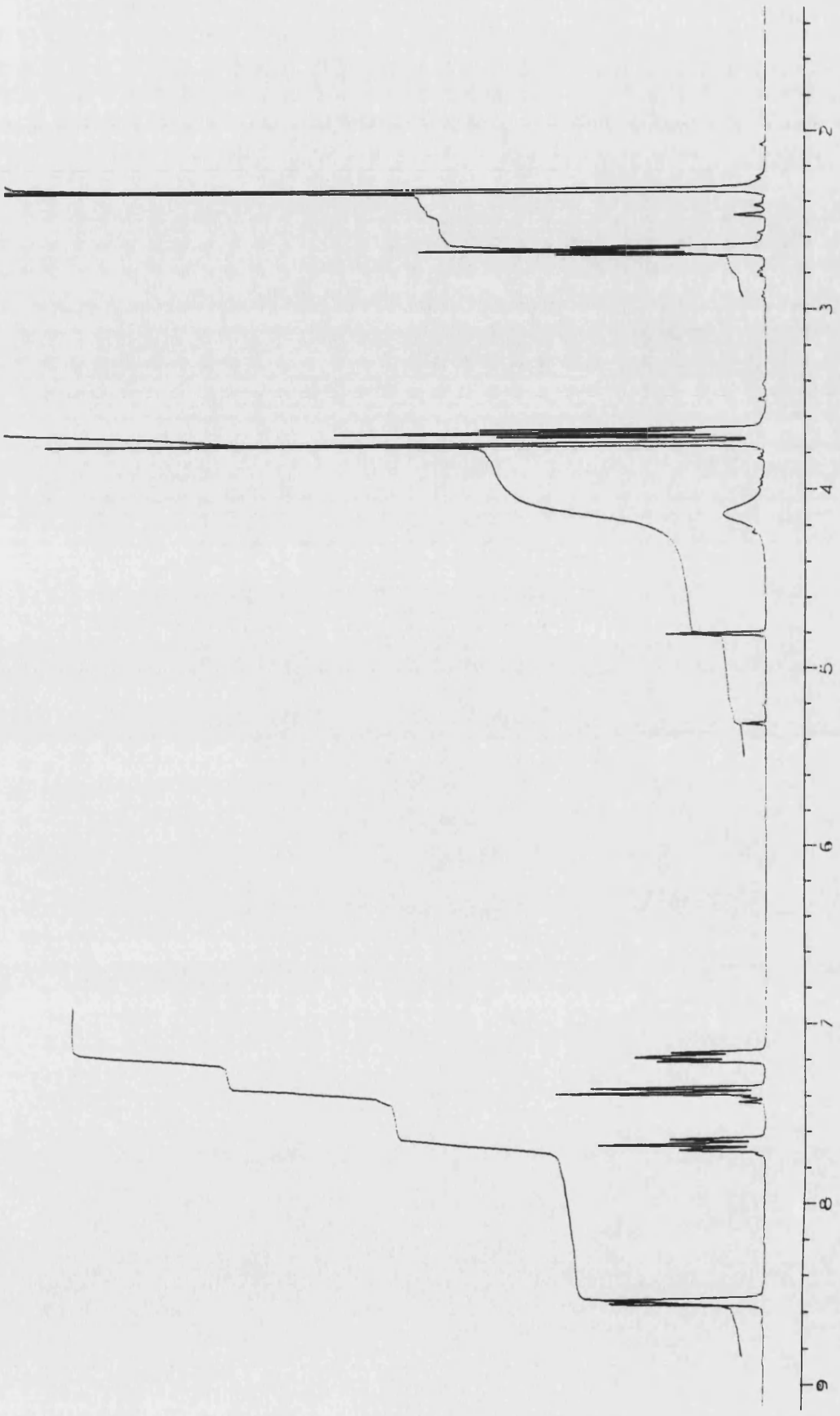


Figure 2.8. ^{1}H NMR spectrum of 5 recorded in $CDCl_3$.

2.2 Organofunctionalised Siloxanes

2.2.1 Introduction

Once a ligand had been suitably functionalised with a 1-alkenyl or hydroxyl-terminated alkyl chain, it was then necessary to determine whether it could be chemically bound to a siloxane backbone containing Si-H moieties *via* either a hydrosilylation, or a dehydrocoupling reaction. An alternative method for introducing ligating functionalities *via* the end-group manipulation of an existing side-arm substituent of a siloxane was also investigated. This methodology provides a potential entry into materials with end-groups which inhibit silylation reactions, or for which precursors containing an alkenyl substituent are difficult to prepare. Thus by reacting a 1-alkenyl chain containing a terminal leaving group, such as a halide or a sulfonate ester, with a Si-H containing siloxane, an intermediate siloxane is formed, which will react with nucleophiles at the *C*-halogen or *C*-ester bond (see **Section 2.2.3**). The main disadvantage of this procedure is the susceptibility of the Si-O-Si backbone to nucleophilic attack, resulting in cleavage of an Si-O bond.

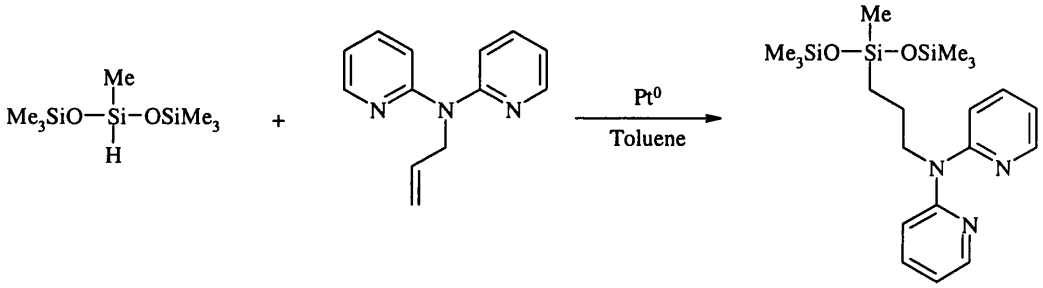
This section describes the synthesis, and attempted synthesis, of organofunctionalised siloxanes using the ligands described previously. In order to isolate discrete compounds and define reaction conditions, initial investigations were made using the model trisiloxane, 1,1,1,3,5,5,5-heptamethyltrisiloxane, Hmts. One other benefit of using Hmts is that it has a boiling point of 142°C and so can be mostly removed from a reaction mixture under reduced pressure, so facilitating the isolation of the desired product in a pure state.

2.2.2 Reactions of Acyclic N-Donor Ligands with Hmts

2.2.2.1 Prdpa

Initial attempts to functionalise Hmts with **1** utilised the platinum(II) catalyst, $[Pt(cod)Cl_2]$. On heating Hmts with **1** in toluene at 85°C, for 24 h, in the presence of this catalyst, it was

found that no reaction had occurred. A similar procedure using the alternative catalyst, $[Rh_2(cod)_2Cl_2]$, also failed. It was eventually found that the Pt(0) catalyst, platinum divinyltetramethylsiloxane, $[Pt^0_2(CH_2{=}CH)(Me)_2Si]_2O)_3]$ (also called the Karstedt catalyst), catalysed the desired hydrosilylation reaction under the conditions described above. After first distilling off the solvent and unreacted starting materials from the reaction residue, the organofunctionalised trisiloxane 3-(2,2'-dipyridyl(*N*-propyl)amino)-1,1,1,3,5,5,5-heptamethyltrisiloxane, (Prdpa)Hmts, **6**, was isolated by distillation at higher temperature, as a viscous, yellow oil in low overall yields (29%), Scheme 2.8.



Scheme 2.8. Synthesis of 6.

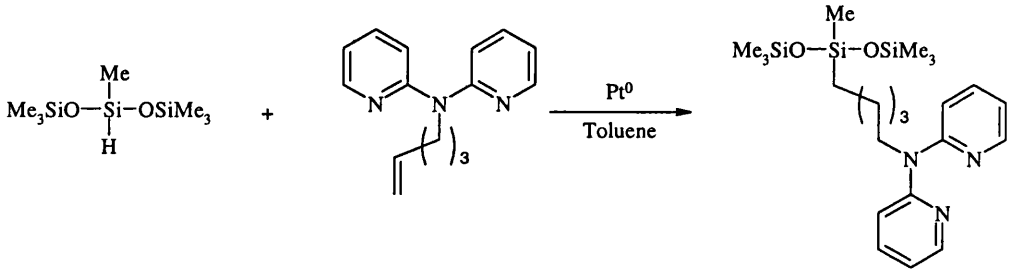
The increased reactivity of the Pt(0) catalyst compared with either the Pt(II) or Rh(I) complexes may result from the metal already being in the zero oxidation state as required for Pt catalysed hydrosilylations, and from its solubility in fluid siloxanes.[26]

The ^1H and ^{13}C NMR spectra of **6** show the changes expected on attachment of the ligand to the siloxane. Thus the proton signals associated with the -CH=CH_2 unit of the alkenyl group are replaced by two signals corresponding to saturated methylene groups at $\delta = 0.52$ (Si-CH_2) and 1.73 (-CH_2-) ppm. In the ^{13}C NMR spectrum these two methylene carbons resonate at $\delta = 14.9$ and 21.8 ppm. These are typical values for such Si-CH_2-CH_2 linkages in other organofunctionalised trisiloxanes.[27,28,29] The *N*-CH_2 group of **6** is no longer affected by the electron withdrawing -CH=CH_2 moiety of the alkenyl group, and the signal appears at $\delta = 4.86$ ppm in the ^1H spectrum (*cf.* $\delta = 4.15$ in the free ligand), and $\delta = 51.3$ ppm in the ^{13}C spectrum (*cf.* $\delta = 50.3$ in the free ligand).

The ^{29}Si NMR spectrum showed the two expected signals corresponding to the two equivalent $Si(CH_3)_3$ (δ = 7.0 ppm) groups and the central $(CH_3)Si(O)_2$ (δ = -21.7 ppm) moiety. There were no other signals in the spectrum, indicating that the alkenyl functionality of **1** adds to the Si-H moiety of Hmts in an *anti*-Markownikoff fashion, as observed in many other hydrosilylation reactions.[28,30]

2.2.2.2 Pedpa

Attempts to functionalise Hmts with Pedpa *via* a hydrosilylation reaction using $[Pt(cod)Cl_2]$ as the catalyst also failed, but the model trisiloxane, 3-(2,2'-dipyridyl(*N*-pentyl)amino)-1,1,1,3,5,5,5-heptamethyltrisiloxane, (Pedpa)Hmts, **7**, was synthesised in moderate yields using the Karstedt catalyst, Scheme 2.9. The higher yield of **7** as compared to **6** is a good indication that lengthening the alkenyl chain from propenyl to pentenyl does indeed aid in the hydrosilylation of the Rdpa unit.



Scheme 2.9. Synthesis of 7.

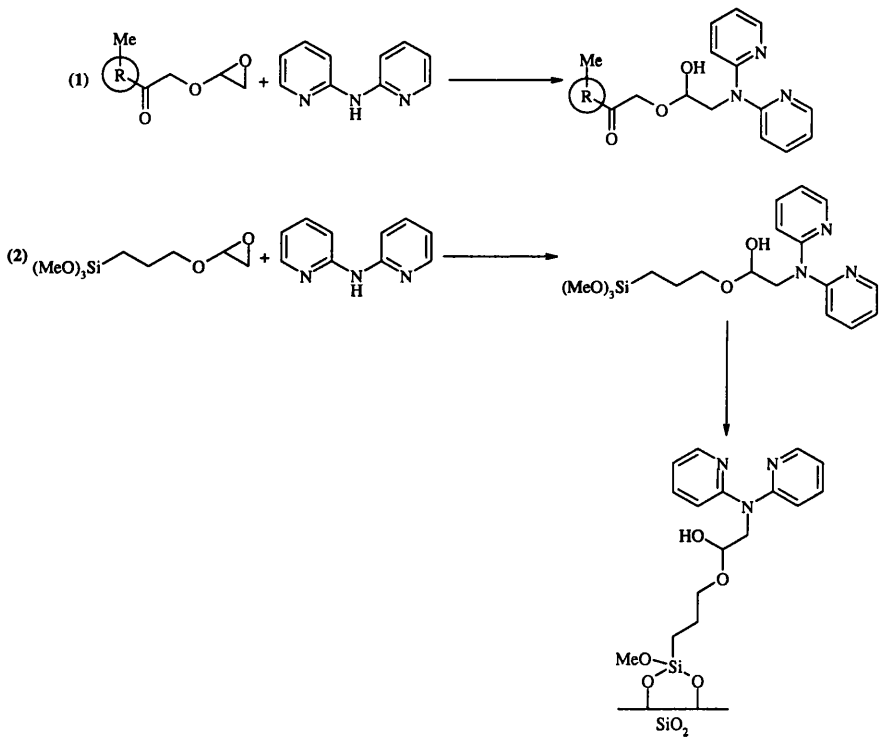
Isolation of **7** was achieved after filtration to remove the Pt residues, and removal of solvent under reduced pressure, by distilling the unreacted ligand and trisiloxane from the reaction residue under reduced pressure. As **7** is less volatile than **6**, it could not be distilled, but remained as a yellow oil.

Both the ^1H and ^{13}C NMR spectra of **7** showed very little change in the chemical shifts of the signals associated with the pyridyl rings or the Si-Me groups. The *N*-CH_2- triplet at δ = 4.20 ppm in the free ligand now appears at δ = 4.15 ppm in the ^1H NMR spectrum of the functionalised siloxane. This methylene carbon resonates at δ = 48.4 in **7** (*cf.* δ = 47.8 ppm in **2**) indicating that the length of the spacer chain is such that conversion of the terminal

alkene group to a saturated Si-C chain has a minimal electronic effect on the *N*-CH_2 group. A more marked electronic effect is reflected in the chemical shifts of the protons of the methylene units β and γ to the tertiary amine. In the free ligand these are highly influenced by the alkenyl moiety but on hydrosilylation they appear with lower δ values of 1.36 ppm and 1.71 ppm respectively. The Si-CH_2 linkage in **7** resonates at δ = 0.46 ppm, which is of a similar value to that found for **6** and other similarly functionalised trisiloxanes.[27-29]

The ^{29}Si NMR spectrum of **7** shows only two signals, at δ = -21.4 and 6.79 ppm, indicating that, as with **6**, only the *anti*-Markownikoff addition product is formed.

The Rdpa moiety has very recently been attached to methacrylate based polymer resins *via* an epoxide ring-opening reaction. These materials were then used after metallation as supported catalysts for the hydrolysis of the nerve agent Sarin.[31] The Rdpa unit has also been attached to a (trimethoxy)(alkyl)silane using a similar methodology, and the intermediate was used to functionalise a silica surface for ion exchange materials, Scheme 2.10.[32] This epoxide ring opening reaction provides another potential method for

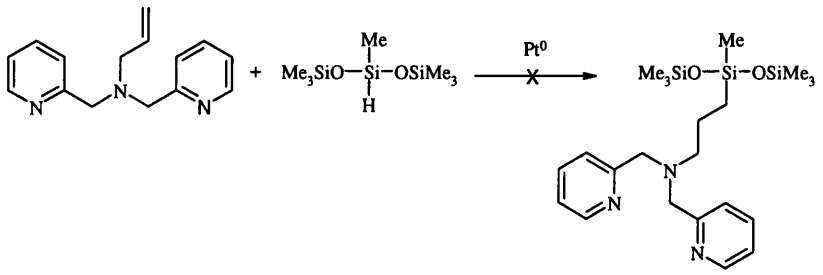


Scheme 2.10. Rdpa functionalised organic (1) and inorganic (2) solids.

introducing the Rdpa unit to siloxane membranes but it has not been reported as far as we are aware.

2.2.2.3 Prbmpa

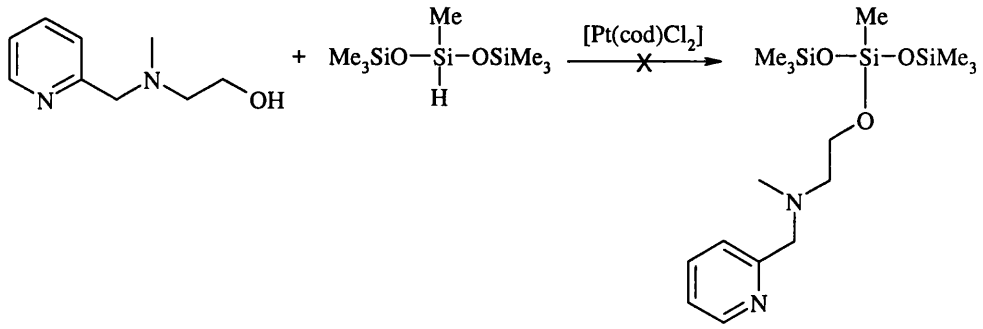
Attempts to hydrosilylate **3** using the Pt^0 based Karstedt catalyst were unsuccessful, Scheme 2.11. The reaction conditions were the same as those used for the hydrosilylation of **2** and **3** (24 h at 85°C in toluene), but on removal of the solvent and volatile materials under reduced pressure Prbmpa was recovered quantitatively.



Scheme 2.11. Attempted reaction between Hmts and 3.

2.2.2.4 Mamp

The reaction between a Si-H group and a primary alcohol is generally facile and will progress without the need of a catalyst. It is, however, a slow reaction and a catalyst is usually added to increase the rate of reaction. Attempts were made to bind **5**, which contains a hydroxyalkyl unit, to the model trisiloxane, Hmts. Initially the reaction was attempted using solvent free conditions, with the catalyst $[Pt(cod)Cl_2]$ first dissolved in **5** before mixing with Hmts. The reaction mixture was heated to 85°C for 48 hours but no reaction occurred. As the siloxane and the ligand are immiscible even at elevated temperatures, the reaction was attempted twice more using the same catalyst but adding increasing amounts of toluene as the solvent. Surprisingly the ligand did not react with the siloxane, Scheme 2.12, although very similar reactions catalysed by $[Pt(cod)Cl_2]$ have been reported in the literature.[33]

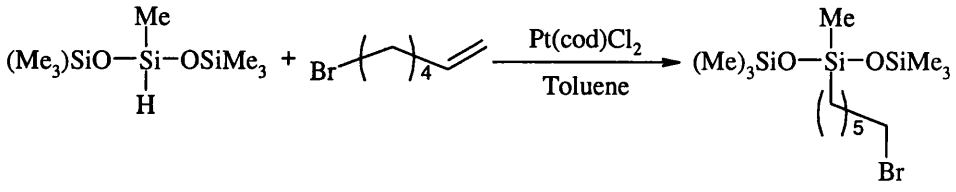


Scheme 2.12. Attempted reaction between 5 and Hmts.

2.2.3 End Group Manipulation

In an effort to develop an alternative route for ligand attachment to Hmts, end group manipulation of a functionalised trisiloxane was attempted. Other investigators have successfully used this procedure to convert terminal -CN to CO_2H groups for example.[34] By adding an alkenyl chain with a terminal leaving group to the trisiloxane, nucleophilic displacement using a protic ligand, LH, or its salt L^- affords a possible route to new organofunctional materials.

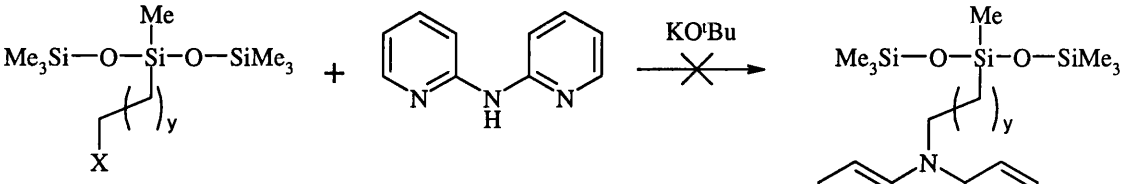
The model compound 1,1,1,1,3,5,5,5-heptamethyl-3-(6-bromohexyl)-trisiloxane, (BrHex)Hmts, **8**, was isolated in good yields by reacting 6-bromo-1-hexene with Hmts using $[Pt(cod)Cl_2]$ as the catalyst, Scheme 2.13. It was characterised by both ^1H and ^{13}C NMR data as well as by microanalysis (see **Chapter 6**).



Scheme 2.13. Synthesis of 8.

This trisiloxane was then reacted with an excess of 2,2'-dipyridylamine in the presence of KO^tBu in an attempt to substitute the bromide with the amine (Scheme 2.14) but on working up the reaction mixture none of the required product was evident.

The reaction was repeated using a better leaving group. To this end, the sulfonate ester dec-9-enyl-4-methylbenzenesulfonate, **9**, which was synthesised in 64% yield from 9-decen-ol and tosyl chloride (see **Chapter 6**), was reacted with Hmts to form the substituted organo-siloxane (Tosdec)Hmts, **10**. This was then reacted as above using the same reaction conditions but again no reaction was observed, Scheme 2.14. Although there is the potential for nucleophilic attack on the Si-O-Si backbone rather than on the side chain, there was no positive indication that this happened under the conditions used.



X = Br, Y = 5;
X = OTs, Y = 7.

Scheme 2.14. Attempted functional group manipulation.

2.3 Membranes Containing Dispersed Solids.

An alternative method for the incorporation of catalytically active, or absorbent species, in poly(siloxane) membranes is to simply disperse finely divided solids into the poly(organosiloxane) fluid before casting the membrane itself. Due to the lipophilic nature and high permeability of siloxanes, a chemical or nerve agent could be absorbed or rendered inactive by a reactive species present in the membrane. In this instance there is no chemical link between the ligand system and the siloxane backbone, but a heterogeneous rather than a homogeneous material will result. Investigations were therefore undertaken to demonstrate this approach by incorporating either an absorbent (carbon), a reactive non-metal (treated silica), or metal containing solids ($Cu(OH)_2$ and $Zn(OH_2)$) into poly(siloxane) membranes.

The species to be incorporated were either provided as powdered solids by the project sponsor (DERA), or were finely ground by hand. A known weight of the solid was mixed thoroughly with a weighed sample of α,ω-poly(disilanol) (MW = 18,000 Daltons), and prior to pressing the membrane, this dispersion was mixed with PMHS, $Si(OEt)_4$ and then

dibutyltin dilaurate catalyst, to initiate the cross-linking process as described in **Section 1.3.6**. Full details for this process are given in **Section 6.0.4.2** and the membranes that were produced during this investigation (**11-30**) are noted in **Chapter 6, Table 6.1**. Several of the membranes produced in this study were sent to DERA and were subjected to evaluation against mustard gas.

2.3.1 Carbon and Silica Containing Membranes (11-16)

It was found that by simply hand mixing carbon with the silanol, a homogeneous distribution of solid in the final membrane could not be guaranteed. To try to introduce a greater level of homogeneity, some exploratory attempts were made into dispersing standard carbon black in the fluid disilanol using a sonication bath prior to cross-linking. This improved the level of homogeneity but did not completely eliminate aggregation.

The use of a sonic horn was next investigated. However it was found that the initial mixture of PDMS and carbon was too viscous to allow cavitation to occur, thus preventing any degree of mixing. By using a less viscous, lower molecular weight (MW = 4,200 Daltons) silanol terminated PDMS this problem was solved and cavitation of the suspension of carbon in PDMS now occurred. Samples were sonicated for either 12 or 30 minutes. This lower molecular weight polymer could be used on its own as a cross-linker, or in conjunction with the higher molecular weight disilanol. After cross-linking and pressing the membranes showed an increase in homogeneity but a completely uniform dispersion was still not achieved. The degree of homogeneity did not appear to be affected by the length of time the sample was sonicated. It seems likely that the low density of powdered carbon makes it difficult to disperse evenly.

Silica loaded membranes were more easily prepared, and hand mixing sufficed to produce viable membranes. As silica greatly increased the viscosity of even the lower molecular weight disilanol sonication was not a viable method of dispersion at even low loadings.

2.3.2 Copper(II) and Zn(II) Hydroxide Containing Membranes (17-23)

Membranes containing metal salts were prepared by hand mixing as for silica. The membranes produced with dispersed $Zn(OH)_2$ were uniformly opaque but otherwise unremarkable. However, after pressing the $Cu(OH)_2$ containing membranes were brown. After curing for 48 h at 90-100°C the colour changed to green and remained this colour. Reduction of Cu(II) to Cu(I), followed by air oxidation of the copper complex at elevated temperatures was suspected. Heterosiloxane formation, which is known to occur in reactions of poly(siloxanes) with some other metals is another possibility.[35] Although compounds containing Si-O-Cu bonds are known, they are rare.[36]

Further investigations showed that there was no colour change when powdered $Cu(OH)_2$ was dispersed separately in either a silanol terminated PDMS or in $Si(OEt)_4$. When PHMS and $Cu(OH)_2$ were stirred together under nitrogen the initial light blue colour of copper(II) hydroxide changed to dark green after 20 minutes. Exposure to air, and heating at 50°C for 2 h caused no further change. (**NOTE**. In the presence of strong bases PHMS decomposes and evolves H_2 at a dangerously high rate at elevated temperature, consequently this reaction was carried out with due care.) Extraction of unreacted PHMS with CH_2Cl_2 left a gelatinous green solid, which showed characteristic IR absorbances for Si-H and -OH bonds

This experiment was repeated with the addition of a few drops of dibutyltindilaurate catalyst. After approximately 10 minutes of stirring, and exposure to the atmosphere, the mixture had turned brown and after 2 hours the fluid had solidified into an intractable, black, porous, heterogeneous solid. X-ray powder diffraction showed that the final solid was not crystalline. IR measurements indicated that Si-H (2171 cm^{-1}) and Si-O-Si (1100 cm^{-1}) bonds were present. The lack of -OH absorbances suggests that new Si-O-Cu bonds may also have been formed, but in view of the intransigent and heterogeneous nature of the solid the experiment was abandoned.

It appears that PHMS reacts with $Cu(OH)_2$, but that the brown colouration developed in the membrane requires the presence of the dibutyltindilaurate catalyst. The dispersion of

ligand stabilised copper(II) derivatives in siloxane membranes by an identical procedure to that described above can be achieved without change in the identity of the complex.[37]

2.4 Conclusions

The bidentate ligands Prdpa and Pedpa have both been synthesised in low yields by reacting the corresponding 1-alkenyl halide with deprotonated 2,2'-dipyridylamine. A similar procedure was also used to synthesise the functionalised tridentate ligand Prbmpa from Hbmpa. The latter was better prepared from the reductive amination of 2-picolylamine and 2-pyridinecarboxylate, rather than from the reaction of 2-picolylamine with 2-picolylchloride hydrochloride. Attempts to synthesise the pentenyl homologue of Prbmpa were not successful. The Mamp ligand, which contains one pyridyl and one tertiary *N*-donor moiety terminated with a hydroxyl chain, was prepared in good yields from the reaction of 2-picolylchloride hydrochloride and *N*-methyl-ethanolamine.

Both Prdpa and Pedpa have been hydrosilylated with the trisiloxane Hmts to form the functionalised siloxanes (Prdpa)Hmts and (Pedpa)Hmts respectively. A Pt(0) catalyst was necessary for this reaction and the larger alkenyl chain on Pedpa facilitated hydrosilylation. Attempts to functionalise Hmts with Prbmpa *via* hydrosilylation, and with Mamp *via* a dehydrocoupling reaction, failed and resulted in quantitative recovery of the starting ligands Attempts to develop an alternative route for ligand attachment to Hmts by nucleophilic displacement of a reactive end-group on side arm functionalised siloxanes were unsuccessful.

A range of cross-linked poly(siloxane) membranes formed by the reaction of PHMS with an α,ω-disilanol and $Si(OEt)_4$ and containing known loadings of dispersed carbon, silica, $Cu(OH)_2$ or $Zn(OH)_2$ were made. Neither hand-mixing nor sonication were effective in producing a homogeneous dispersion of carbon whereas viable silica and $Zn(OH)_2$ containing films could be produced readily by dispersing the solids in the reactant silanol. Membranes containing $Cu(OH)_2$ changed colour from blue to brown on cross-linking, and then to green after heating and exposure to the atmosphere. It seems likely that reduction to an intermediate Cu(I) species by the siloxane is followed by slow reoxidation to Cu(II).

2.5 References.

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Chapter 3:

Cyclic *N*-Donor Ligands.

Chapter 3: Cyclic *N*-Donor Ligands

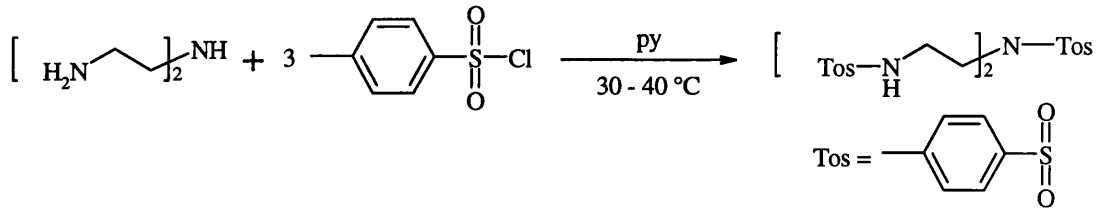
3.0 1,4,7-Triazacyclononane, H_3tacn 86
3.0.1 Synthesis of $[H_6tacn]Cl_3$, 27 86
3.1 The Functionalisation of H_3tacn 90
3.1.1 The Synthesis of Symmetrically *N*-Functionalised R_3tacn 91
3.1.2 Symmetrically Substituted Alkenyl Derivatives of H_3tacn 92
3.1.2.1 1,4,7-Tri(*N*-propenyl)-1,4,7-triazacyclononane, Pr_3tacn, 28 92
3.1.2.2 1,4,7-Tri(*N*-pentenyl)-1,4,7-triazacyclononane, Pe_3tacn, 29 95
3.1.3 Trisubstituted H_3tacn Containing a Hydroxyl-Terminated Alkyl Chain 98
3.2 The Synthesis of Mono-Substituted H_3tacn Derivatives 100
3.3 Attempted Preparation of Cyclic *N*-Donor Ligand Functionalised Trisiloxanes 105
3.3.1 Pr_3tacn and Pe_3tacn 105
3.4 Conclusions 108
3.5 References 109

3.0 1,4,7-Triazacyclononane, H_3tacn

The ligand 1,4,7-triazacyclononane, H_3tacn, has been shown to be an important ligand in designing model compounds for dioxygen activating enzymes (see **Section 1.2**). To this end, investigations were undertaken into the syntheses of this ligand, and appropriately functionalised derivatives, to make it suitable for attachment to oligo-, and poly(siloxanes). Due to the prohibitive cost of H_3tacn the quaternary ammonium salt $[H_6tacn]Cl_3$, was first synthesised from simple, and inexpensive starting materials.

3.0.1 Synthesis of $[H_6tacn]Cl_3$, 27

Using the methodology described by Atkins,[1] the tris-sulfonamide, 1,4,7-tris(*p*-tosyl)diethylenetriamine, **24**, was isolated, in high yields (71%), as a dark yellow solid, following the reaction of diethylenetriamine with three equivalents of *p*-tolylsulfonyl-chloride (TosCl), in pyridine at 30-40°C, Scheme 3.1. By protecting the amine groups with the bulky, aromatic sulfonamides rotation around the NCH_2CH_2N linkages is slowed, thus enhancing the likelihood of ring closure rather than polymerisation.

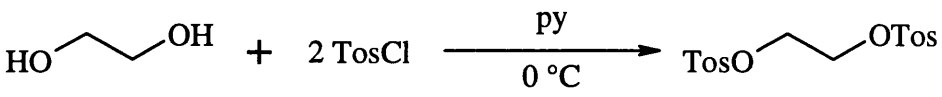


Scheme 3.1. Synthesis of 24.

The observed ^1H and ^{13}C NMR data for **24** are in good agreement with those reported in the literature[2] with one exception. Soriano *et al* reported that the secondary amine protons resonated as a multiplet at δ = 5.30 ppm.[2] In the course of this study however, this signal was not observed in our spectra, despite the spectra being recorded in the same deuterated solvent. However, the identity of the compound and the presence of the N-H group, was confirmed by IR and microanalytical data.

In order to effect ring closure of the linear triamine a suitable 1,2-disubstituted ethane is required. Early synthetic procedures utilised 1,2-dihaloethanes, usually the bromide, in high dilution.[3] The method described by Atkins[1] however, utilises a 1,2-di-sulfonate ester derivative, synthesised from 1,2-ethanediol (ethylene glycol). This methodology provides a better leaving group and so gives higher yields with the need for the reaction to be performed in high dilution. Yields of the cyclic product are also better and separation from any polymeric material is facile.

The required 1,2-disulfonate-ester, diethylene glycol ditosylate, **25**, was formed by the reaction between ethylene glycol and two equivalents of TosCl, in pyridine, held at 0°C for 2 h, in accordance with the literature procedure.[4] The product was isolated after recrystallisation in 85% yield, Scheme 3.2.



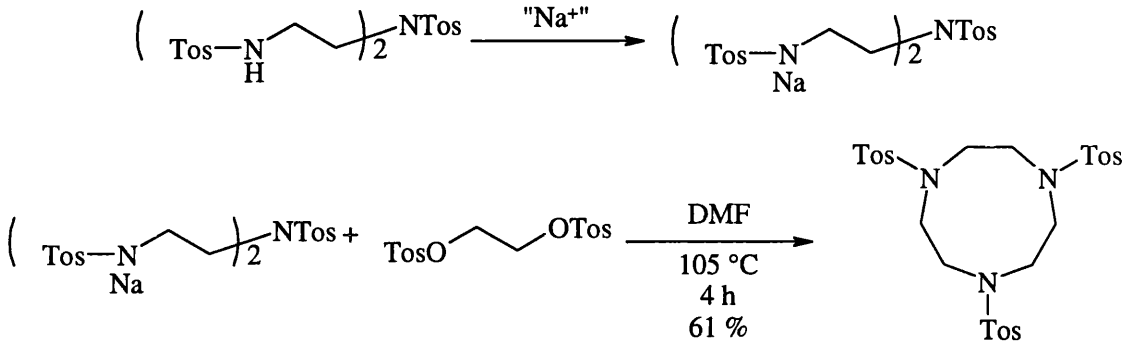
Scheme 3.2. Synthesis of 25.

The ^{1}H and ^{13}C NMR data for this compound are readily assigned due to the high degree of symmetry in the molecule, and our data are in good agreement with those reported in the literature.[5]

The ring closure reaction, to give the tri-sulfonamide protected macrocycle, 1,4,7- tris(*p*-tolylsulfonyl)1,4,7-triazacyclononane, **26**, was performed using one of the two methods, as summarised in Scheme 3.3, and described in more detail below.

- The reaction as described by Hay and Govan,[6] first involves the isolation of the disodiumsalt of **24** by direct treatment with sodium ethoxide in ethanol. This is subsequently dissolved in DMF and reacted over 5 hours with **25**.
- The second method is a modification to the first. Instead of isolating the disodium salt of **24**, it is formed *in situ*, by reacting the linear tri-sulfonamide with an excess of sodium hydride in DMF. After removal of unreacted sodium hydride the reaction proceeds as in Method **1**.

An overall yield of **26** of *ca.* 60% was obtained by either method. The *in situ* formation of the disodium salt, however, has been found by the author to be the more convenient. The ^{1}H (Figure 3.1) and ^{13}C NMR data for **26** are in good agreement that in the literature.[7]



Scheme 3.3. The synthesis of 26.

Conversion of the cyclic tri-sulfonamide to its corresponding hydrochloride salt $[H_6tacn]Cl_3$, **27**, proved difficult due to conflicting synthetic procedures and imprecise experimental details given in the literature. All three methodologies detailed below, were attempted numerous times before the desired product was finally isolated.

- The methodology first described by Wieghart involves treating the tris-sulfonamide **26** with 47% aqueous HBr, and isolating the cyclic triamine as the trihydrobromide salt.[3] A variation of this method has also been published that included the addition of a small quantity of glacial acetic acid to the aqueous HBr solution.[8]
- The deprotection of both linear and macrocyclic *p*-toluenesulfonamides, including **26**, has been accomplished in only 6-8 minutes, in 50% sulfuric acid at 180°C according to another report.[9] It was found in this investigation that dissolution of **26** did not occur, and no reaction took place under these conditions.
- Another method that has been cited in the literature is a radically initiated conversion of a sulfonamide to the corresponding amine using SmI_2.[10] Attempts to use this methodology in this investigation led to quantitative recovery of the starting material **26**.

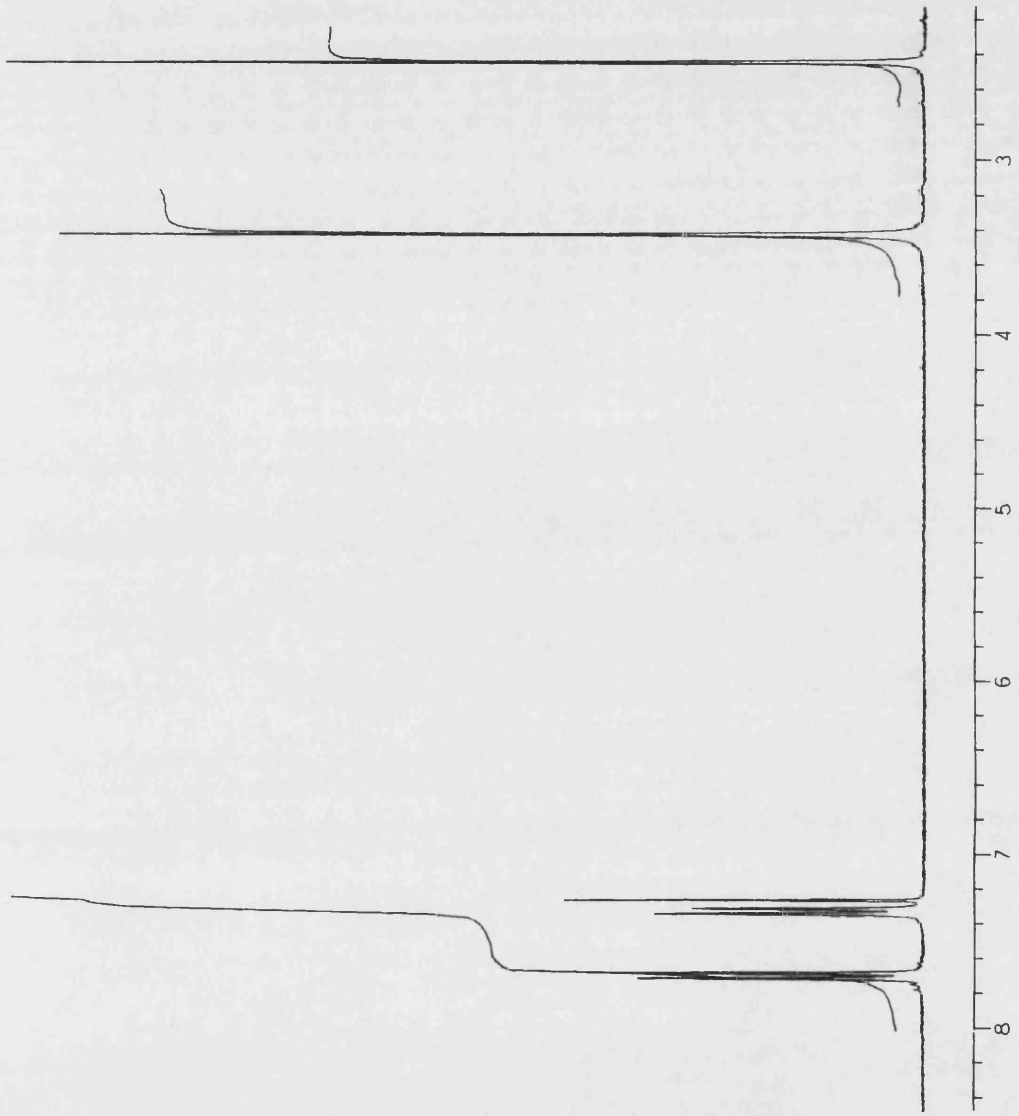
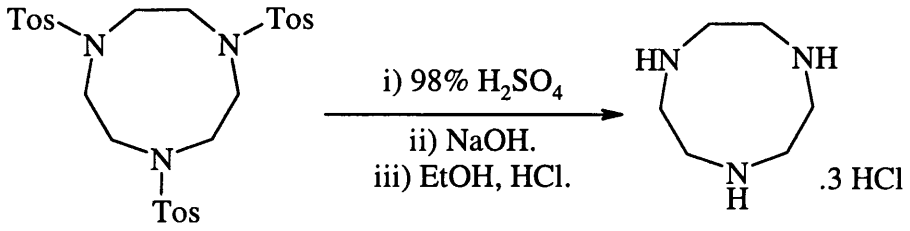


Figure 3.1. ^{1}H NMR spectrum of 30 recorded in $CDCl_3$.

After considerable experimentation it was found that the deprotection step (Scheme 3.4) could be achieved, using a modification of a fourth procedure, as described by Hay.[6] After heating a solution of **26** in concentrated (98%) H_2SO_4, at 120°C, for 72 h, the strongly acidic solution was carefully made alkaline to pH 14, and the crude hydrosulfate salt was extracted into $CHCl_3$. At a pH lower than 14 the product remains highly water-soluble and cannot be extracted into the organic solvent. This procedure removes the need for the continuous extraction techniques at neutral pH as reported by Hay[6] and other researchers.[11]

On removal of the solvent, the residue was dissolved in ethanol, and after removal of any insoluble material by filtration, the tri-hydrochloride salt $[H_6tacn]Cl_3$, **27**, was precipitated by addition of a slight excess of concentrated HCl (~10 M). After recrystallisation from 2 M HCl/EtOH, the trihydrochloride salt isolated in moderate yield (55%).



Scheme 3.4. Deprotection of 26 to 27.

Both the ^1H and ^{13}C NMR data for **27**, recorded in D_2O, each show only one resonance, at $\delta = 3.35$ and $\delta = 45.0$ ppm respectively (lit. values: $\delta = 3.70$ and $\delta = 41.8$ ppm in D_2O[7]). The protons of the quaternary amine salt are not observed in the ^1H NMR spectrum due to rapid exchange with deuterons present in the solvent.

3.1 The Functionalisation of H_3tacn

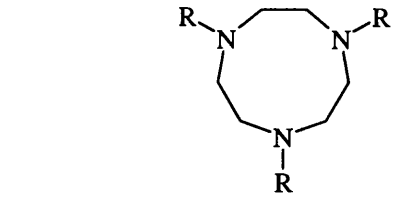
In order to make H_3tacn suitable for attachment to a Si-H moiety, one or more of the three secondary amines need to be functionalised with a spacer chain terminated by a $-CH_2=CH_2$, or -OH moiety. The synthesis of these substituted ligands can be approached in one of two ways:

- Functionalisation of all three N-H centres would allow the R_3tacn unit to be attached to up to three Si-H units and simultaneously act as a cross-linking agent for polymeric siloxanes.
- Functionalisation of a single N-H group would allow the tacn unit to be attached to just one Si-H group to produce a side-arm functionalised siloxane.

The synthetic methods used to produce compounds of both types are described below.

3.1.1 The Synthesis of Symmetrically N-Functionalised R_3tacn

The functionalisation of H_3tacn has been the subject of two comprehensive reviews.[12,13] Whilst much attention has been focussed on the tri-*N*-methyl derivative, Me_3tacn,[14] many investigations have also centred on the inclusion of three substituents which themselves contain functional groups. Figure 3.2 summarises some of these substituents which include carboxylate,[15] amino,[16] hydroxyl,[17] phosphino,[18] sulfonate[19] and pyridyl[20] end groups.



R = $-CH_2COOH$; $-CH_2CH_2NH_2$; $-CH_2CH_2OH$;
$-CH_2P(C_6H_5)_2$;$-CH_2CH_2SO_3H$;

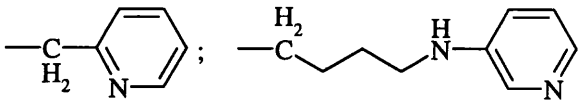


Figure 3.2. Symmetrically functionalised tacn derivatives.

Much of the chemistry described in the literature performed on H_3tacn uses the free base as a starting material. In these investigations the starting material was the trihydrochloride salt. As the presence of water is undesirable for many reactions, attempts were first made to neutralise the quaternary salt without resorting to the use of an aqueous solvent system.

It was found that the salt could be conveniently converted into the free base by suspending it in either dry acetonitrile or dry diethyl ether, and adding either a stoichiometric quantity of triethylamine, NEt_3 or stirring with excess solid KOH. Both $[NHEt_3]Cl$ and KCl are insoluble in ether and were easily removed by filtration. However, $[NHEt_3]Cl$ has a slight solubility in MeCN, and consequently the use of KOH was generally preferred.

3.1.2 Symmetrically Substituted Alkenyl Derivatives of H_3tacn

Two different alkenyl chains, 1-propenyl and 1-pentenyl, have been added to H_3tacn to form 1,4,7-tris(propenyl)-1,4,7-triazacyclononane, **28**, and 1,4,7-tris(pentenyl)-1,4,7-triazacyclononane, **29**, respectively.

3.1.2.1 1,4,7-Tri(*N*-propenyl)-1,4,7-triazacyclononane, Pr_3tacn, 28

A number of different conditions and solvent systems, as summarised in Table 3.1, were used in attempts to synthesise **28**, by reacting **27** with allyl bromide in the presence of base. Until the development of a successful procedure, each time the reaction was attempted the only product isolated was a brown oil, soluble in CH_2Cl_2, which contained nitrogen but could not be converted to a quaternary salt on addition of aqueous acid.

Solvent	Base Used	Reaction Temperature	Stoichiometry (allyl bromide:tacn)
H_2O/EtOH/Tol.	KOH	R.T.	3.5:1
MeCN	KOH	85°C	3:1
MeCN	NEt_3	85°C	3.5:1
MeCN/Tol.	KOH	85°C	3:1

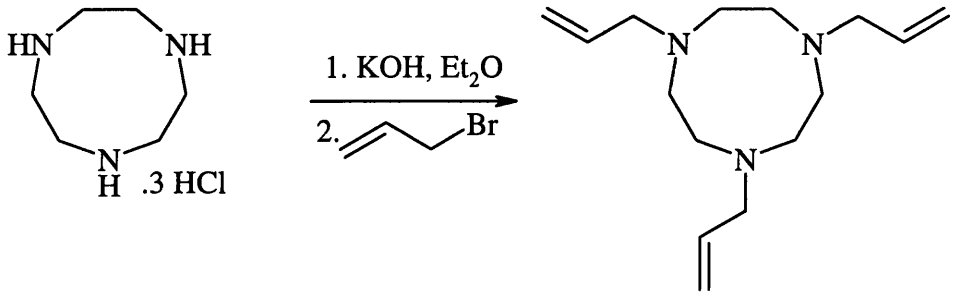
Table 3.1. Conditions used in the attempted reaction between 27 and allyl bromide

The ^{1}H NMR spectrum of the product isolated consisted of 4 signals indicating the presence of both macrocyclic and allylic protons. However, the relative intensity ratio of the signals for the ring to allyl substituent protons was 1:1 and not 2:1 as expected for the

desired tri-substituted product. This observation indicates that symmetrical quaternisation of the amines may have occurred. Moreover, an aqueous solution of this oil immediately gave a precipitate of AgBr on treatment with acidified $AgNO_3$, also indicating that quaternisation of one or more of the amine groups may have occurred. The only reported quaternary ammonium salt of a R_3tacn derivative that has been reported is $[Me_6tacn][BF_4]_3$, which is formed by the extensive methylation of the tri-methyl derivative, Me_3tacn.[21] No NMR data were reported for this compound to allow comparison with the spectra of the alkenylated product isolated in this study, and further investigations are required to fully characterise the species isolated.

After some considerable investigations **28** was eventually prepared using one of the three different synthetic methods as described below.

- Initially an ethereal solution of the free base of **27**, formed using the NEt_3 method, was treated with an excess of sodium hydride. After removal of unreacted NaH, allyl bromide was added to the reaction mixture containing Na_3tacn, which was stirred for 2 h. After work up, **28** was isolated in low yields.
- A modification of the procedure developed by Peacock *et al.* for the synthesis of 1,4,7-tris-(3-prop-1-yne)-1,4,7-triazacyclononane was also used successfully.[22] The free base dissolved in toluene/EtOH (1:1) was stirred over KOH and subsequently reacted with allyl bromide. After removal of volatiles the required product, **28**, was extracted into dry Et_2O and isolated in moderate yields.
- In a modification of procedure 2, **27** suspended in Et_2O was stirred with KOH to liberate the free amine before treatment with a slight excess of allyl bromide. Any quaternary salt present, together with KBr, precipitated leaving only **28** in solution which was finally isolated in 80% yields, Scheme 3.5.



Scheme 3.5. Synthesis of 28.

Due to the efficiency of the third method it was possible to use **28** directly for synthetic purposes, without further purification. It was, however, purified by distillation for complete analytical characterisation.

The ^{1}H NMR spectrum of **28** is shown in Figure 3.3. The macrocyclic NCH_2CH_2N protons appear as a singlet at $\delta = 2.75$ ppm. The *N*-methylene protons of the propenyl chain appear as a doublet at $\delta = 3.14$ ppm, whilst those of the $-CH=CH_2$ unit resonate at $\delta = 5.10$ (CH_2) and 5.89 (CH) ppm. The chemical shifts of the macrocyclic protons and the methylene spacer for **28** are comparable with those of 1,4,7-tris-(3-prop-1-yne)-1,4,7-triaza-cyclononane, Pry_3tacn, which resonate at $\delta = 2.72$ (see Table 3.2) and 3.37 ppm respectively.[22]

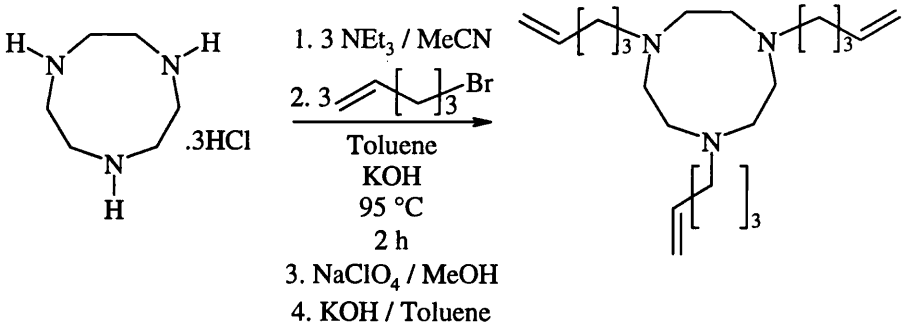
The ^{13}C NMR data for **28** also consists of only four signals. The ring carbons appear at $\delta = 55.3$ ppm whilst signal from the three carbons of the allyl chain occur at $\delta = 61.9$ ($N\text{-}CH_2$), 116.4 (CH_2) and 136.8 (CH) ppm. The value for the macrocyclic carbons is similar to that observed for Pry_3tacn ($\delta = 53.6$ ppm).[22]

The tri-substituted ligand Pr_3tacn has been mentioned in previous reports but neither its synthesis nor characterisation has so far been published.[25,23,.24] The mono-substituted ligand, PrH_2tacn and the disubstituted ligand, $Pr_2Metacn$,[25] have also both been reported previously. The former was synthesised using the methodology first described by Atkins.[26] Initially H_3tacn is "capped" and the orthoamide isolated is reacted with allyl bromide. (This methodology is discussed later in more detail in **Section 3.2**). The final product was isolated in low yields after removal of the "cap" by hydrolysis. $Pr_2Metacn$ synthesised in two stages using an extension of this method.

3.1.2.2 1,4,7-Tri(*N*-pentenyl)-1,4,7-triazacyclononane, Pe_3tacn, 29

Attempts to synthesise **29** using the methodology developed by Wieghardt *et al* for the synthesis of the tri-*N*-isopropyl derivative[27] did not yield the desired product, but after modification this method was used successfully for the preparation of the tris-*N*-pentenyl derivative **29**.

A suspension of **27** in dry acetonitrile was first converted to H_3tacn by treatment with 3 equivalents of triethylamine. After removal of solid $[NHEt_3]Cl$, the filtrate was diluted with toluene (this also had the effect of precipitating any $[NHEt_3]Cl$ still remaining in solution) and the cyclic triamine reacted with 3 equivalents of 5-bromo-1-pentene in the presence of KOH, Scheme 3.6. After work up **29** was purified by conversion into its hydro-perchlorate salt $[Pe_3tacnH][ClO_4]$, which could be easily isolated and converted back to the free amine when required.



Scheme 3.6. The synthesis of 29.

The ^1H NMR data for **29** are as expected. The ring methylene protons in **28**, **29** and other $(R'CH_2)_3tacn$ derivatives[22,28-31] exhibit very similar chemical shifts (Table 3.2) and the δ values of the $-CH=CH_2$ protons (δ_{CH_2} = 4.98 ppm and δ_{CH} =5.82 ppm) are also similar to those of **28**. The resonance for the *N*-methylene protons in **29** is shifted by *ca.* 0.6 ppm relative to that in **28** by the two methylene spacer units in the former. For comparative purposes the chemical shift of *N*-methylene protons is the two alkynylated compounds Pry_3tacn[22] and Pey_3tacn[28] are given in Table 3.2. The remaining signals at δ = 1.54 and 2.07 ppm in the spectrum of **29** are assigned to these two methylene units.

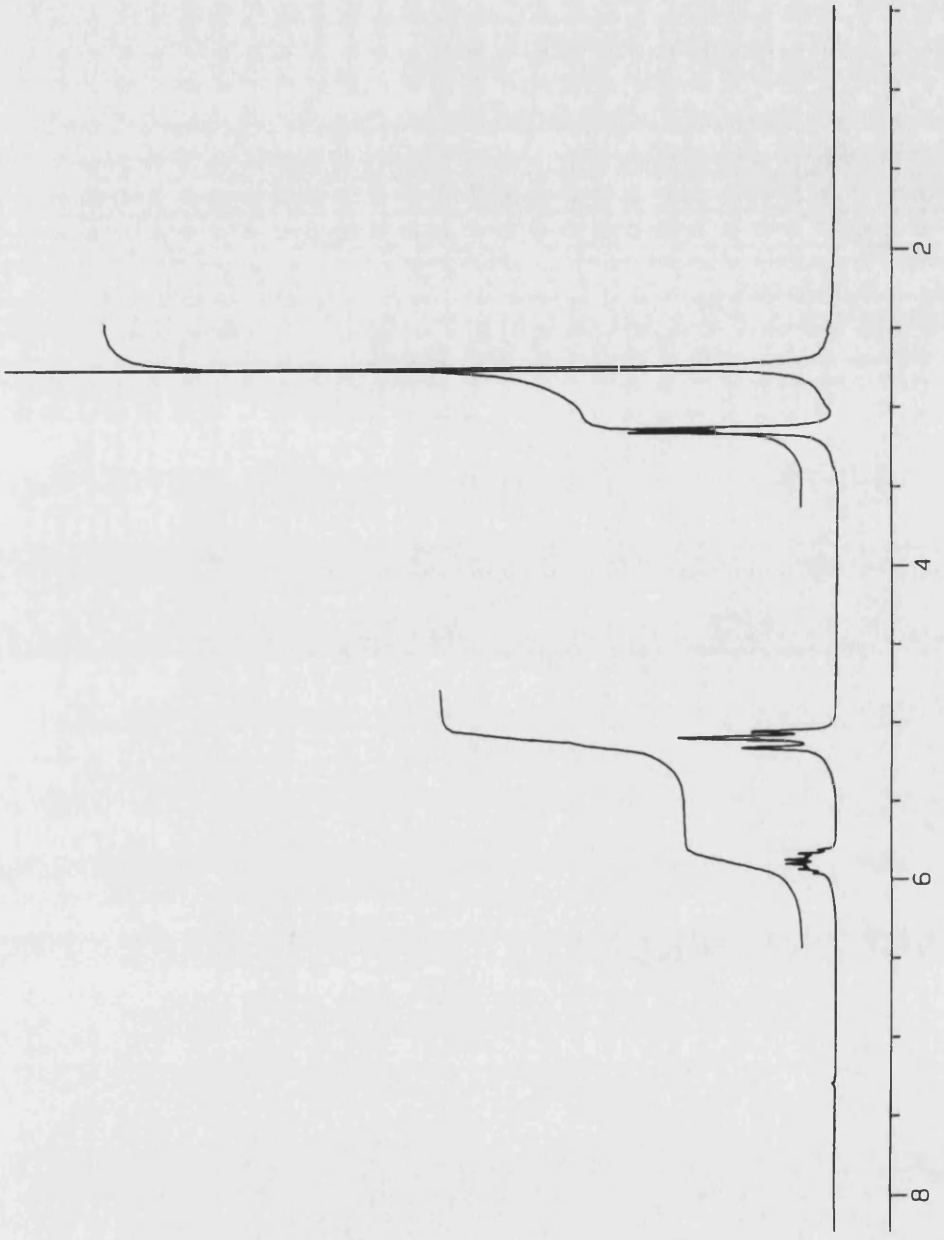


Figure 3.3. ^{1}H NMR spectrum of 28 recorded in $CDCl_3$.

The ^{13}C NMR data for **29** are also as expected. The most significant change in chemical shift compared with **28** occurs for the exocyclic *N*-methylene carbons ($\delta = 31.7$ ppm compared to $\delta = 61.9$ ppm for **28**).

The chemical shifts of the ring methylene and exocyclic *N*-methylene protons of both **28** and **29** are compared in Table 3.2 with a selection of other R_3tacn derivatives. The substituents have very little effect on the ring protons, but a significant effect is noted for the chemical shifts of the exocyclic *N*-methylene group.

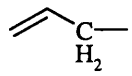
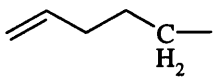
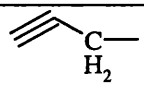
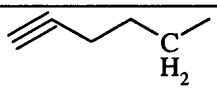
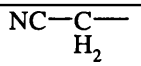
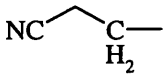
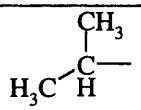
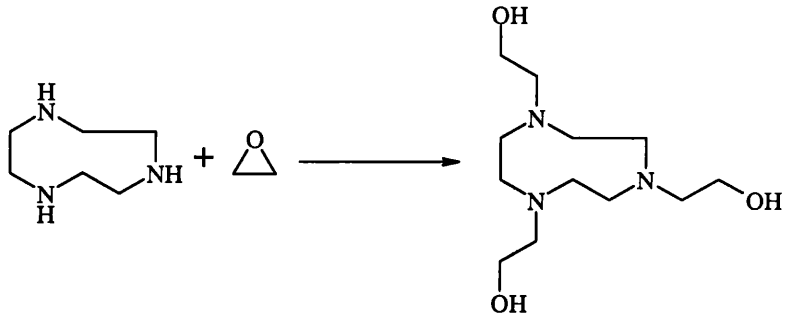
R	$\delta_{NCH_2CH_2N}$ / ppm	δ_{NCH_2} (acyclic) / ppm	Solvent	Reference
H	2.82	N/A	$CDCl_3$	7
	2.75	3.14	$CDCl_3$	**Section 3.1.2.1**
	2.72	2.47	$CDCl_3$	**Section 3.1.2.2**
	2.72	3.37	$CDCl_3$	22
	2.70	2.56	$(CD_3)_2CO$	29
	2.85	3.59	$CDCl_3$	30
	2.79	2.86	$CDCl_3$	30
	2.72	N/A	$CDCl_3$	31

Table 3.2. Comparison of the substituent effect on the chemical shift of *N*-methylene protons of R_3tacn.

3.1.3 Trisubstituted H_3tacn Containing a Hydroxyl-Terminated Alkyl Chain

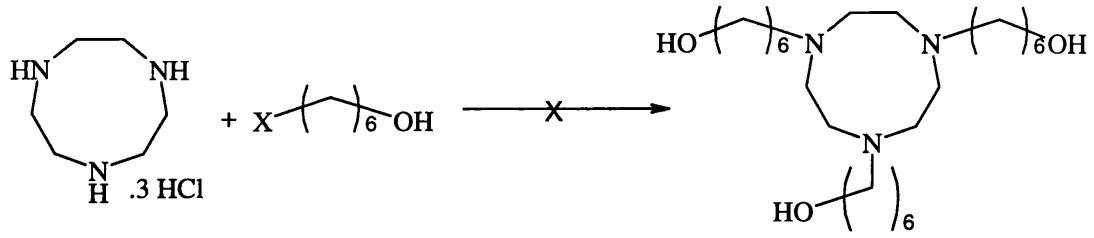
Several attempts were also made to synthesise a R_3tacn derivative containing a *N*-bonded spacer chain terminated by a hydroxyl group, which could be used to functionalise siloxanes. However, all, as described below, were unsuccessful.

The only tri-functionalised H_3tacn derivative containing a primary alcohol functionality that we are aware of in the literature is 1,4,7-tri(hydroxyethyl)triazacyclononane.[17] This is formed in high yield by the reaction between H_3tacn and ethylene oxide, Scheme 3.7. Ethylene oxide is difficult to handle, only available commercially in relatively large quantities, and the reaction generates a shorter spacer chain than is desirable for subsequent reaction with a Si-H moiety. For these reasons routes to longer spacer chain materials were briefly investigated.



Scheme 3.7. Synthesis of 1,4,7-tri(hydroxyethyl)triazacyclononane.

The direct reaction between H_3tacn and 1-chloro- and 1-bromo-6-hexanol, Scheme 3.8, was attempted numerous times, first using the procedure used successfully for the synthesis of both Pr_3tacn and Pe_3tacn, and then varying the conditions. None of the desired product was formed and the halohydrin was invariably isolated quantitatively after work up.

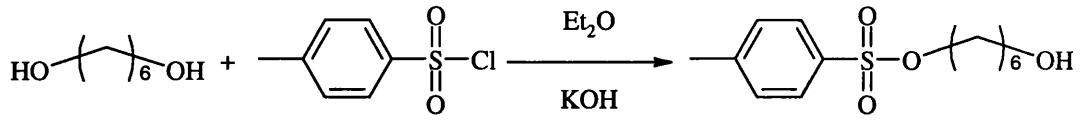


X = Cl or Br

Scheme 3.8. Attempted syntheses of a trisubstituted H_3tacn containing a primary alcohol group.

The reaction between a halohydrin and the di-tosyl protected macrocycle, Tos_2Htacn, was reported by Sessler in 1993 for the preparation of $(Tos)_2(HO(CH_2)_3)$tacn.[32] An excess of 3-bromopropanol was used in acetonitrile in the presence of less than one equivalent of NEt_3. This procedure was followed using H_3tacn instead of the diprotected macrocycle in an attempt to functionalise all three N-H groups, but again no reaction occurred and the halohydrin was recovered in near quantitative amounts.

An alternative route to the desired compound involving the reaction of H_3tacn with the mono-sulfonate ester of a diol was attempted. As the sulfonate is a better leaving group than halide, it is more susceptible to nucleophilic attack. The compound 1-tosyl-6-hexanol, **30**, was successfully synthesised by reacting 1,6-hexanediol with TosCl in Et_2O, Scheme 3.9.



Scheme 3.9. Synthesis of 30.

This compound was then heated with H_3tacn in aqueous ethanol. After work up the ^{1}H NMR spectra of the final residue revealed signals characteristic of both the triazacyclononane and the primary alcohol but not in the expected intensity ratios, and no pure product could be isolated. The reaction was not pursued further in favour of a different approach.

3.2 The Synthesis of Mono-Substituted H_3tacn Derivatives

The synthesis of mono-substituted H_3tacn compounds usually proceeds *via* a selective deprotection of Tos_3tacn to Tos_2Htacn or $TosH_2$tacn, followed by functionalisation of one or two of the amines, then deprotection, of the remaining amine moieties, Figure 3.4.

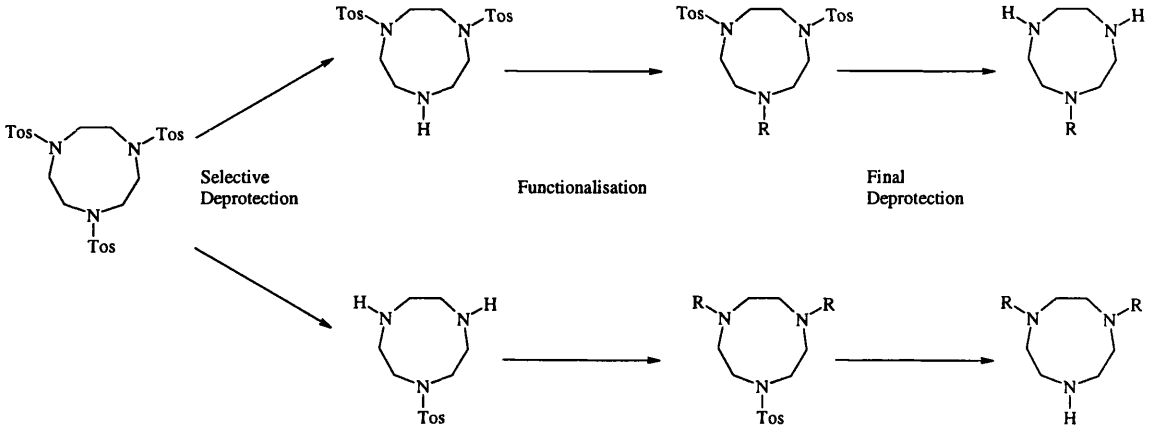
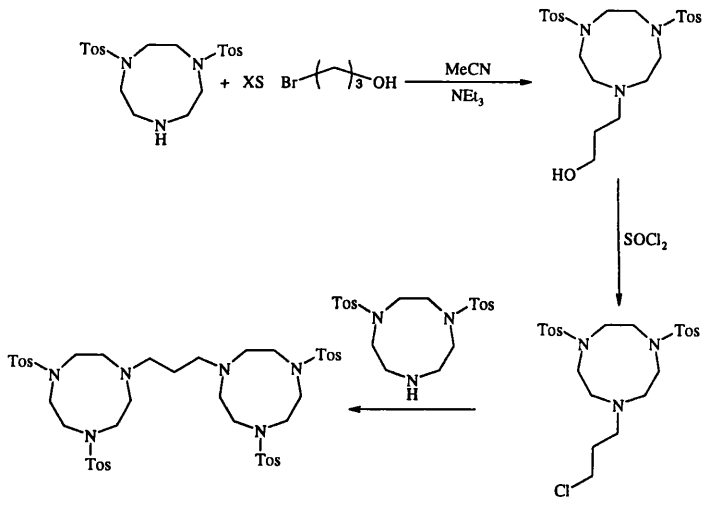


Figure 3.4. Selective functionalisation of H_3tacn using selective deprotection.

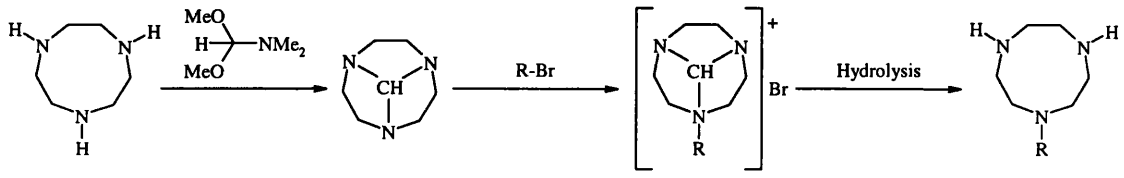
As noted above Sessler *et al* used this approach successfully to synthesise a mono-functionalised H_3tacn derivative containing an alkyl chain terminated by a primary alcohol.[32] This product was subsequently used to form a bis-macrocycle as shown in Scheme 3.10.



Scheme 3.10. Sessler's reaction between Tos_2Htacn and 3-bromopropanol.

As the conversion of the sulfonamide groups to secondary amines requires the use of concentrated H_2SO_4, only substituents that are not affected by these conditions can be introduced. Consequently this route is unsuitable for the selective addition of a single alkenyl or hydroxyalkyl chain to H_3tacn as either functionality would be affected under the harsh deprotection conditions needed to remove the tosyl groups.

An alternative route to mono-functionalised derivatives involves the conversion of H_3tacn to its ortho-amide derivative by reaction with dimethylformamide dimethylacetal.[26] The "capping" of the macrocycle then allows substitution at only one of the nitrogens to occur on reaction with an alkyl halide. A quaternary ammonium salt is formed, which on hydrolysis affords the monofunctionalised amine, Scheme 3.11. This method is more widely applicable, as the hydrolysis conditions are relatively mild.

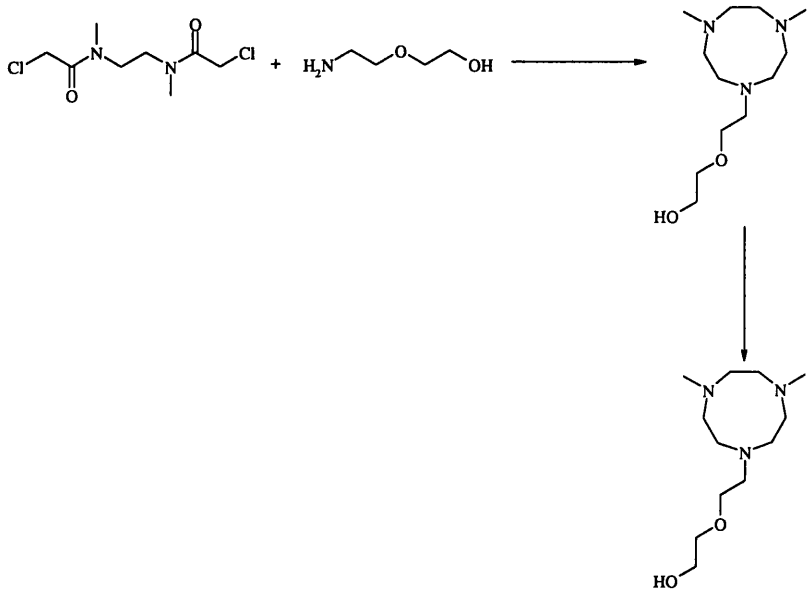


Scheme 3.11. Selective functionalisation of H_3tacn *via* a cyclic ortho-amide.

The route described above was also attempted but the initial orthoamide could not be isolated.

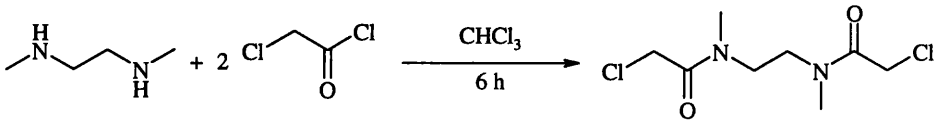
In a final attempt to prepare the desired mono-functionalised triazamacrocycle a cyclisation reaction was carried out in which the required substituent was already present on one reactant.

Bradshaw *et al* cyclised a primary amine containing a primary alcohol functionality with a linear diamide to afford a cyclic diamide.[33] On reduction this gave a tacn derivative with a pendant chain containing a primary alcohol terminus. The series of reactions needed to isolate this compound are outlined in Scheme 3.12.



Scheme 3.12. Synthesis of a mono-functionalised H_3tacn derivative.

The first step in the synthesis of 1-(2-ethoxy)hydroxyethyl-4,7-dimethyl-1,4,7-triazacyclononane, Hedmtacn, as shown in Scheme 3.12, involves the formation of the known diamide *N,N'*-di(2-chloroacetyl)-*N,N'*-dimethylethylenediamine, **31**.[34] This pale yellow product was formed in good yields (62%; lit. yield = 75%[34]) by reacting *N,N'*-dimethyl-ethylenediamine with chloroacetylchloride in refluxing $CHCl_3$, Scheme 3.13, using a modified literature procedure.[34]

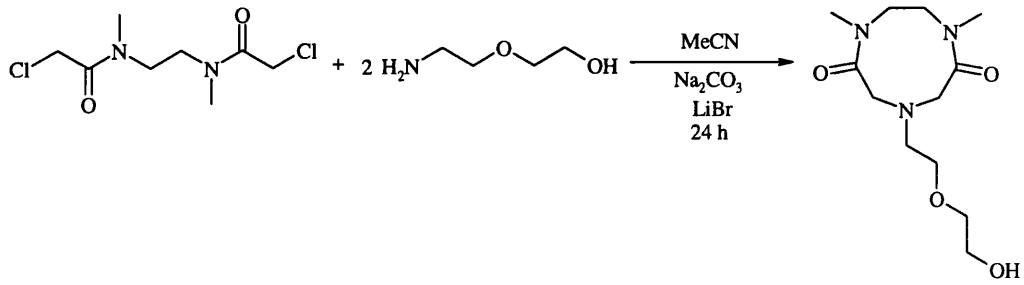


Scheme 3.13. Synthesis of 31.

The ^{1}H NMR spectrum of **31** is quite unremarkable and consists of three separate singlets at δ = 3.13, 3.61 and 4.05 ppm which are assigned to the *N*-C<u>H</u>$_3$, *N*-C<u>H</u>$_2$ and C<u>H</u>$_2$-Cl protons respectively. The ^{13}C NMR spectrum of **31** is also readily assigned with the signals at δ = 36.0 (*N* -<u>C</u>H$_3$), 41.4 (*N*-<u>C</u>H$_2$), 45.2 (<u>C</u>H$_2$-Cl) and 167.2 (<u>C</u>=O) ppm. Although the compound has been previously reported,[34] no NMR data have been published.

By reacting **31** with 2-(2-aminoethoxy)ethanol, Aee, in a 1:1 molar ratio, in MeCN in the presence of an excess of Na_2CO_3 the ring closure product 1-(2-ethoxy)hydroxyethyl-3,8-

dioxo-4,7-dimethyl-1,4,7-triazacyclononane **32**, was obtained as a yellow oil, following purification by column chromatography, in low yields. If the reaction is performed using a molar ratio of 2:1, of Aee to **31**, the yield increases to 34%, Scheme 3.14. According to Bradshaw Na_2CO_3 is not a strong enough base to deprotonate the hydroxyl terminal of Aee, but instead deprotonates the amine, which then acts as a better nucleophile than the alcohol derivatives, thus facilitating ring closure.[33]



Scheme 3.14. Synthesis of 32.

The ^1H NMR spectrum of **32** which is reported for the first time, (Figure 3.5), consists of three singlets with chemical shifts of within ±0.1 ppm of those in **31**. The methylene signals of the ether side chain appear as four sets of triplets at $\delta = 2.95$, 3.59, 3.66 and 3.74 ppm.

The ^{13}C NMR spectrum of **32** also shows four signals arising from the four chemically inequivalent methylene units in the side chain. Although all the NMR data correlate well with the structure of **32**, the microanalytical results were not in close agreement with the theoretical values. Attempts at purification did not improve the analyses, but attempts were nevertheless made to complete the reaction sequence.

The remaining step in the reaction involves the reduction of the cyclic amide to the corresponding triamine either using either BH_3•THF or $LiAlH_4$, Scheme 3.15. According to the literature the yield of the cyclic triamine is 40% overall.[33] However, the actual conditions used to perform this reduction were not given, and despite several attempts, the correct conditions needed to effect this reduction cleanly could not be found and the desired product, Hedmtacn, was not isolated.

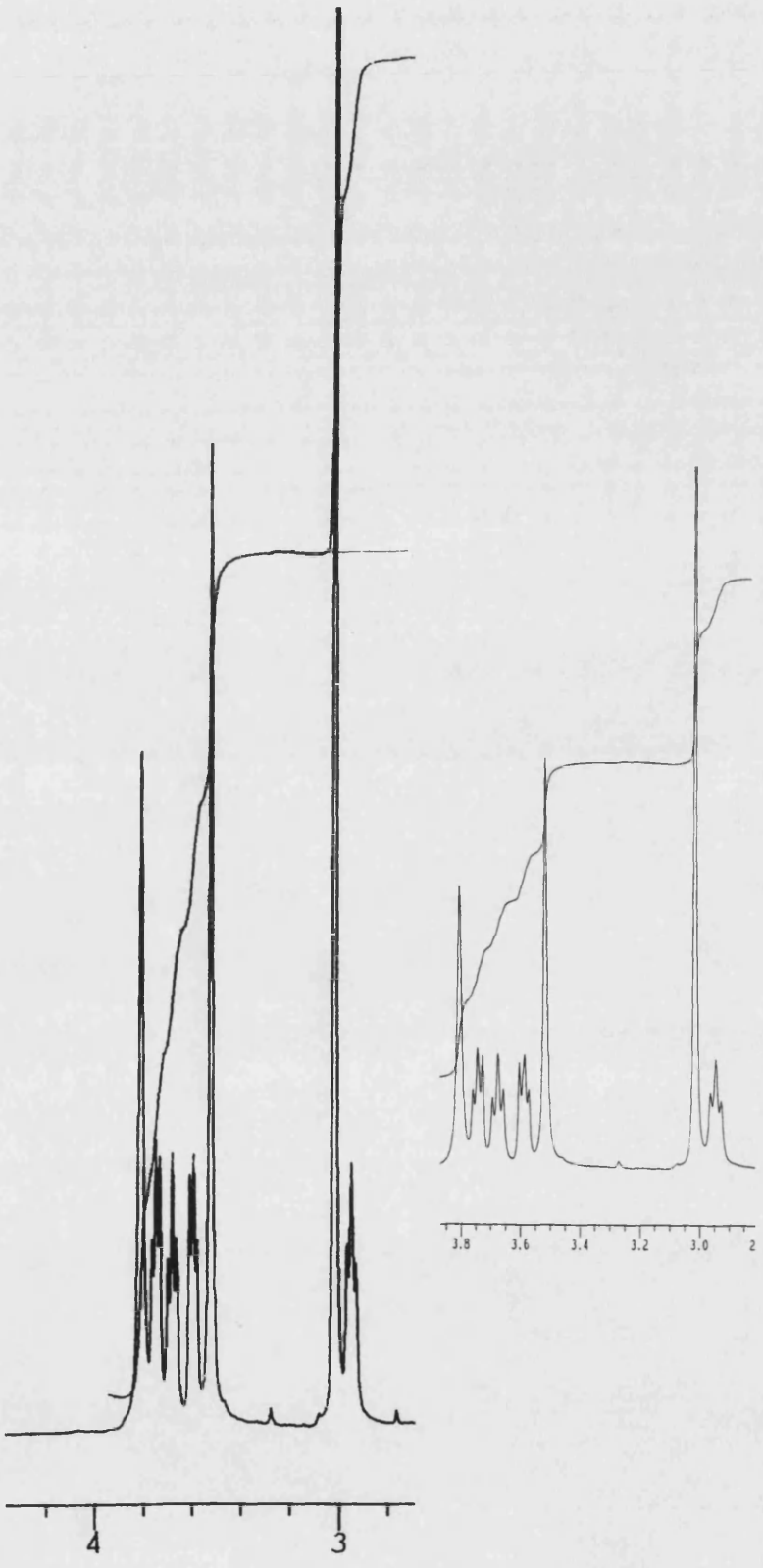
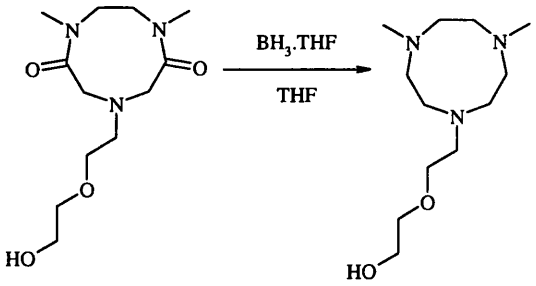


Figure 3.5. ^{1}H NMR spectrum of 32 recorded in $CDCl_3$.



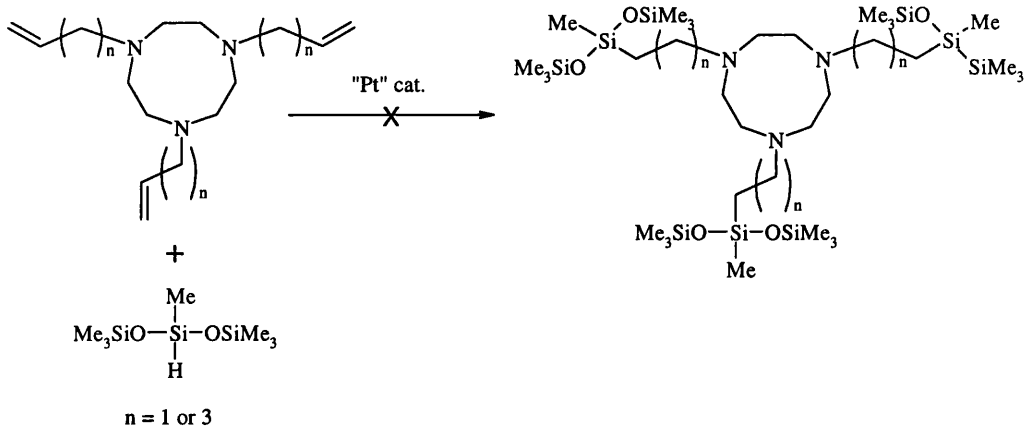
Scheme 3.15. Reduction of 32 to Hedmtacn.

3.3 Attempted Preparation of Cyclic *N*-Donor Ligand Functionalised Trisiloxanes

3.3.1 Pr_3tacn and Pe_3tacn

The presence of three alkenyl chains on the R_3tacn ligands allows up to three hydrosilylation reactions to occur with Hmts to afford the model compounds shown in Scheme 3.16.

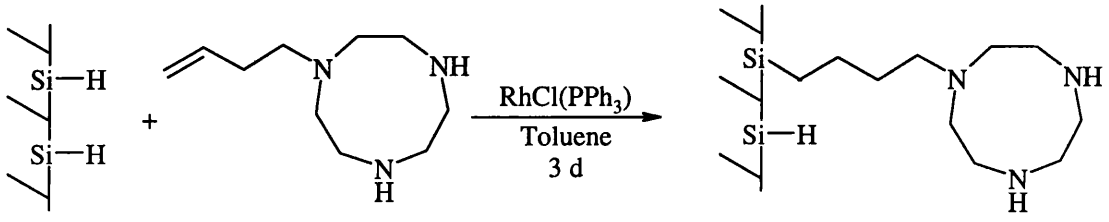
The reactions between Hmts and the two tris-alkenylated species **28** and **29** were attempted numerous times under varying conditions. Both the Pt^{II} and Pt^0 catalysts described earlier (**Chapter 2**) were employed, but neither produced any hydrosilylation product. It is possible that the strongly complexing aza-macrocyclic ligands bind to the Pt catalyst and inhibit the reaction. Complexes of Pt(II) and Pt(IV) with R_3tacn have been previously reported[35] but so far as we are aware no complex formed with Pt(0) has been noted. Further investigations are needed to determine the exact cause of the loss of reactivity of the Karstedt catalyst in this reaction and explore the use of other catalysts (although Pt(0) is generally the most effective catalyst for hydrosilylations involving siloxanes).



Scheme 3.16. Attempted hydrosilylation between 28 and 29 with Hmts.

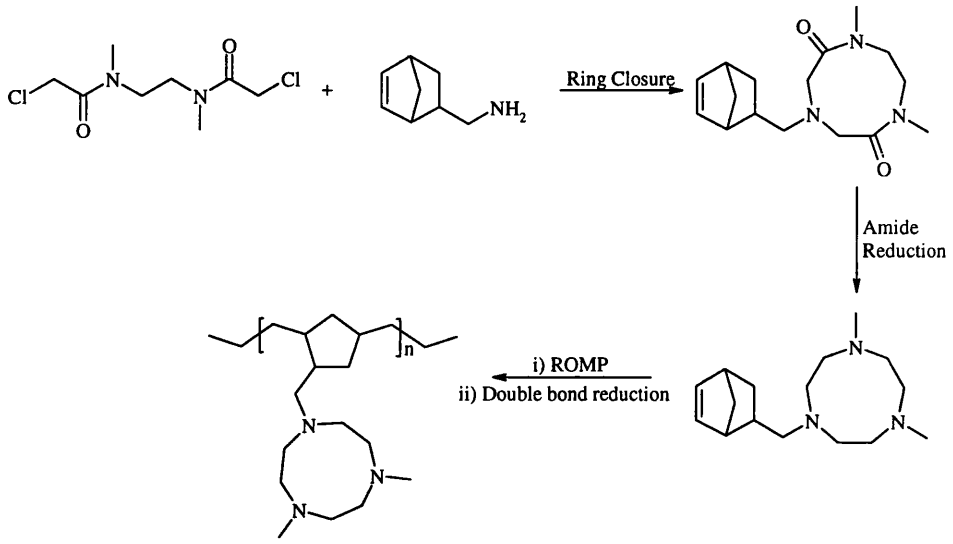
It was noted in **Chapter 1** that radicals formed from either chemical initiators, such as AIBN, or UV light may initiate hydrosilylations. Both methods were employed in an attempt to functionalise Hmts with the R_3tacn ligands (R = Pr or Pe), but again these reactions failed and the ligands were recovered from the reaction mixture.

There is no literature precedent for the attachment of triazacyclononane to a fluid siloxane *via* a hydrosilylation reaction, but both aza-crown ethers,[36] and smaller, pyridyl containing heterocycles have been attached, and the latter metallated with Cu(II) complexes to produce hydroquinone oxidation catalysts.[37] However, a very recent study published after the research described herein was completed, has shown that it is possible to functionalise a silica surface, containing Si-H moieties, with a 1-alkenyl aza-macrocycle by hydrosilylation.[38] Silica suspended in refluxing toluene was reacted for 3 days with *N*-(4-but-1-enyl)-1,4,7-triazacyclononane (prepared using the methodology shown in Scheme 3.11) using $[RhCl(PPh_3)_2]$ as the catalyst, Scheme 3.17. Any Si-H groups that remained were "capped" by hydrosilylating with ethene. The supported ligand was subsequently reacted with $Cu(NO_3)_2$ and the material used as a phosphate diester hydrolysis catalyst.



Scheme 3.17. Functionalisation of a silica surface with R_3tacn *via* hydrosilylation.

It has also been reported in the last few months that an organic polymer can be synthesised bearing a substituted R_3tacn, *via* a ring opening metathesis polymerisation (ROMP), Scheme 3.18.[39]



Scheme 3.18. Functionalisation of an organic polymer with R_3tacn.

3.4 Conclusions

The compound 1,4,7-tris(*p*-tolylsulfonyl)-1,4,7-triazacyclononane was readily isolated in moderate yields from the reaction of the linear protected triamine, 1,4,7-tris(*p*-toluenesulfonyl)diethylenetriamine, and diethylene glycol ditosylate, by following. literature procedures.[1,4,6] Numerous attempts made using various literature procedures to deprotect this compound and isolate the cyclic triamine $[H_6tacn]Cl_3$ were unsuccessful. Deprotection was finally achieved using 98% H_2SO_4, and $[H_6tacn]Cl_3$ was isolated in moderate yields. The free base was functionalised with both 1-propenyl and 1-pentenyl chains. Pr_3tacn was prepared by three different routes, the highest yielding of which involved reacting allyl bromide with $[H_6tacn]Cl_3$ in the presence of base in a non-polar solvent. Pe_3tacn was prepared in moderate yields, using an analogous methodology to that reported by Wieghardt *et al* for the tri-*N*-isopropyl derivative.[27] Attempts to react either Pr_3tacn or Pe_3tacn with Hmts, *via* metal catalysed and radical initiated hydrosilylation, were unsuccessful.

Attempts to *N*-functionalise H_3tacn with 1-hydroxyalkyl chains using halohydrins were unsuccessful. The synthesis of Hedmtacn, which contains an *N*-substituted hydroxyl terminated ether spacer chain was started but not completed. The ring closure product Domtacn, **32**, formed by reacting Aee with **31** in a 2:1 molar ratio, was isolated in moderate yields, but its attempted reduction to the cyclic amine, Hedmtacn, using BH_3·THF, failed.

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Chapter 4:

The Metallation of Ligands.

Chapter 4: The Metallation of Ligands.

4.0 Introduction 114

4.1 Complexes of Acyclic *N*-Donor Ligands 114

4.1.1 2,2'-Dipyridyl(*N*-propenyl)amine, Prdpa 114

4.1.1.1 Copper(II) Nitrate 114

4.0.1.1.1 The Crystal Structure of $[Cu(Prdpa)_2(NO_3)_2]$, 34 118

4.0.1.1.2 The Crystal Structure of $[Cu(Prdpa)(NO_3)_2]$, 35 121

4.0.1.1.3 The Crystal Structure of $[Cu(Hdpa)(NO_3)_2]$, 36 124

4.1.1.2 Copper(II) Chloride 128

4.1.1.3 Zinc(II) Chloride 129

4.1.1.4 Zinc(II) Nitrate 129

4.1.2 2,2'-Dipyridyl(N-pentenyl)amine, Pedpa 134

4.1.3 Summary of Complex Formation between Rdpa and $Cu(NO_3)_2$ 135

4.1.4 Structural Comparisons Between Cu-Rdpa Complexes 136

4.1.5 Bis-2-methylpyridyl(*N*-propenyl)amine, Prbmpa, Adduct 139

4.1.6 2-Methylamino(*N*-methyl-*N*-2-hydroxyethyl)pyridine, Mamp, Adduct 140

4.2 Complexes of Cyclic *N*-Donor Ligands 141

4.2.1 1,4,7-Tri(*N*-propenyl)-1,4,7-triazacyclononane, Pr_3tacn 141

4.2.1.1 Copper(II) Nitrate Adduct 141

4.0.1.1.4 The Crystal Structure of $[Cu(Pr_3tacn)(NO_3)_2]$, 44 143

4.2.1.2 Zinc(II) Nitrate Adduct 146

4.2.2 1,4,7-Tri(N-pentenyl)-1,4,7-triazacyclononane, Pe_3tacn 148

4.2.3 Structural comparison of $[Cu(Pr_3tacn)(NO_3)_2]$ with other Cu-R_3tacn Complexes 149

4.3 Conclusions 153

4.4 References 155

4.0 Introduction

An important aspect of this investigation concerned the identification and structural characterisation of complexes formed between the functionalised ligands and copper(II) and zinc(II) salts. The reason for carrying out structural investigations on the metallated functionalised ligands rather than on the siloxane attached products, is that the latter, although sometimes solids, are invariably amorphous, whereas the former are crystalline. Therefore the determination of a given metal's co-ordination geometry, once it has been attached to a ligand-functionalised siloxane, is not possible using X-ray crystallography, but the structure of the metallated functionalised ligand should reflect the immediate environment of the metal in the siloxane-supported species. X-ray crystallography is also a valuable means of determining whether or not the addition of an alkenyl chain to the ligand significantly alters the co-ordination geometry of its resulting complexes compared with the non-alkenylated ligand which could in turn have implications for catalytic activity. To this end the acyclic bi- and tri-dentate, as well as the cyclic tridentate *N*-donor functionalised, ligands prepared in the course of this investigation (see **Chapters 2** and **3**) were reacted with various copper(II) and zinc(II) salts. Complexes of the latter are significant in catalytic hydrolysis,[1] and in addition their solution behaviour can be probed using NMR spectroscopy.

4.1 Complexes of Acyclic *N*-Donor Ligands

4.1.1 2,2'-Dipyridyl(N-propenyl)amine, Prdpa

4.1.1.1 Copper(II) Nitrate

It was reported in 1964 by McWhinnie that on reacting Hdpa with copper(II) nitrate in acetone, in a 2:1 stoichiometry, a bright green compound precipitated.[2] On recrystallisation of this solid from water, olive green crystals of bis-(2,2'dipyridylamine)copper(II) nitrate, $[Cu(Hdpa)_2(NO_3)_2]$, **33**, were isolated in moderate yields (65%), Scheme 4.1

$$2\ \text{Hdpa} + \text{Cu(NO}_3\text{)}_2 \xrightarrow[\text{ii) } H_2O]{\text{i) Acetone}} [\text{Cu(Hdpa)}_2\text{(NO}_3\text{)}_2]$$
$$\text{RT}$$

Scheme 4.1. Synthesis of 33.

The crystal structure of **33** has since been determined,[3] and the complex was found to exist as mononuclear, neutral units each consisting of a six-co-ordinate copper ion situated at the centre of symmetry of an axially distorted octahedron. The two bidentate Hdpa ligands occupy the equatorial plane, whilst the two monodentate nitrate ligands occupy the axial positions, Figure 4.1. There are also hydrogen bonding interactions present between a nitrate of one unit cell with the N-H moiety of the Hdpa ligand in another unit cell. These interactions extend the mononuclear units into a pseudo-polymer, Figure 4.2.

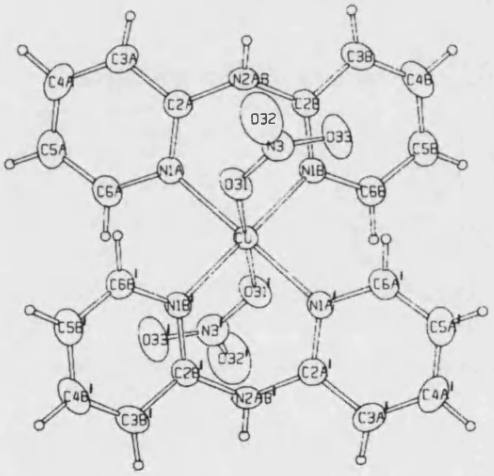


Figure 4.1. Molecular structure of 33.[3(i)]

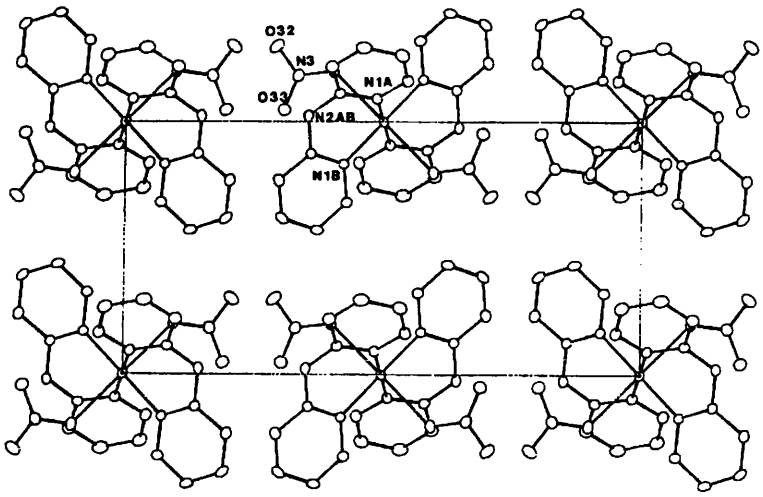


Figure 4.2. Extended lattice structure of 33.[3(i)]

The reaction between Prdpa and $Cu(NO_3)_2$ was performed in order to determine whether replacing the *N*-H of Hdpa by a *N*-alkenyl group would effect the outcome of the reaction. Mixing equimolar quantities of each component, at room temperature in methanol, afforded a dark green solution from which, on standing, a purple solid precipitated which was isolated by filtration. The dark green filtrate that remained was treated with a little Et_2O and cooled, from which a dark green solid separated out from this solution.

The purple solid was recrystallised from boiling methanol and, although good microanalytical results were not obtained for this compound, it was identified by X-ray crystallography (see page 118) as the 2:1 adduct $[Cu(Prdpa)_2(NO_3)_2]$, **34**, isolated in low yields (24%). The green solid was recrystallised from CH_2Cl_2/cyclohexane and was shown by microanalysis to be the 1:1 adduct $[Cu(Prdpa)(NO_3)_2]$, **35**, in low overall yields (12%). It too was structurally characterised by X-ray crystallography (see page 121). The overall reaction is summarised in Scheme 4.2.

This reaction was repeated at 0°C using methanol as the solvent, but with the ligand in a two fold excess. It was found that the purple 2:1 adduct, **34**, was formed in higher yields (66%) under these conditions. The green 1:1 adduct was also formed but only as a minor product. The 1:1 adduct was converted separately to the 2:1 adduct by the addition of a 1 molar equivalent excess of the ligand to a methanolic solution of **35**.

$$3\ \text{Prdpa} + 2\ Cu(NO_3)_2 \xrightarrow[RT]{MeOH} [Cu(Prdpa)_2(NO_3)_2] + [Cu(Prdpa)(NO_3)_2]$$

Scheme 4.2. Synthesis of 34 and 35 in methanol.

The question as to whether or not the formation of both the 1:1 and 2:1 adducts of Prdpa with $Cu(NO_3)_2$ was characteristic only of the *N*-substituted ligand, was answered by repeating McWhinnie's original experiment and undertaking investigations into the unidentified green solid. Microanalysis of this initial product showed it to be the 1:1 adduct $[Cu(Hdpa)(NO_3)_2]$, **36**. The 2:1 adduct, **33**, originally reported by McWhinnie, has two monodentate nitrato ligands present.[2] Nitrato ligand absorptions in the near IR spectrum of **33** were assigned in this investigation at 1019 (ν_{sym}), 1269 and 1468 (ν_{asym}) cm^{-1}. For the bright green 1:1 adduct, nitrato ligand absorptions occur at 1014 (ν_{sym}), 1251 and 1465 (ν_{asym}) cm^{-1}, indicating a change in the co-ordination mode of the ligand. This change was subsequently confirmed by X-ray crystallography as discussed later (see page 124).

Therefore the reaction of Hdpa with copper(II) nitrate in acetone initially produces a 1:1 compound. This undergoes disproportionation in water to form the 2:1 complex, Scheme 4.3.

$$2\ \text{Hdpa} + 2\ Cu(NO_3)_2 \xrightarrow[RT]{\text{Acetone}} 2\ [Cu(Hdpa)(NO_3)_2] \xrightarrow[RT]{H_2O} [Cu(Hdpa)_2(NO_3)_2] + Cu(NO_3)_2$$

Scheme 4.3. Synthesis and disproportionation of 36.

The 1:1 adduct has also been reported as being one of the by-products formed when the analogous nitrito complex, $[Cu(Hdpa)(NO_2)]$ is <u>not</u> recrystallised under a N_2 atmosphere, Scheme 4.4.[4] However, it was noted that bubbling oxygen gas through a methanol, or acetonitrile, solution of the copper-nitrito complex did not yield the corresponding nitrato complex.

$$3\ [Cu(Hdpa)(NO_2)_2] \xrightarrow[\text{Atmosphere}]{\text{Hot MeCN}} [Cu(Hdpa)_2(NO_3)_2] + [Cu(Hdpa)(NO_3)_2] + Cu(NO_3)_2$$

Scheme 4.4. Oxidation of $[Cu(Hdpa)(NO_2)_2]$ to 36.

In order to further explore the solvent dependency of complexes formed between copper(II) nitrate and Hdpa or Prdpa, a number of cross reactions were performed, all using a ligand to metal ratio of 1:1. Firstly the reaction of Prdpa and $Cu(NO_3)_2$ was carried out using McWhinnie's conditions for the formation of the 1:1 Hdpa complex. It was found that only the dark green 1:1 adduct, **35**, precipitated from solution, Scheme 4.5.

$$\text{Prdpa} + Cu(NO_3)_2 \xrightarrow[RT]{\text{Acetone}} [Cu(\text{Prdpa})(NO_3)_2]$$

Scheme 4.5. Synthesis of 35 from acetone.

Methanol was then used as the solvent for the reaction between Hdpa and copper(II) nitrate. On addition of diethyl ether to the reaction mixture the bright green 1:1 complex, **36**, precipitated which could be recrystallised unchanged from methanol. Thus we concluded that the reaction between Rdpa (where R = H or propenyl) and $Cu(NO_3)_2$ when performed in acetone favours the formation of a 1:1 adduct. However, in alcohol, when R = propenyl the 2:1 adduct is the more favoured product and is formed from the disproportionation of $[Cu(\text{Prdpa})(NO_3)_2]$. An alcoholic solution of the 1:1 adduct $[Cu(\text{Prdpa})(NO_3)_2]$ can also be converted to $[Cu(\text{Prdpa})_2(NO_3)_2]$ by addition of a second equivalent of the ligand. When R = H, the 1:1 adduct is the only product isolated when the reaction is carried out in alcohol or acetone. In this instance the disproportionation of $[Cu(\text{Hdpa})(NO_3)_2]$ to the corresponding 2:1 adduct is brought about by the addition of water.

4.0.1.1.1 The Crystal Structure of $[Cu(Prdpa)_2(NO_3)_2]$, 34

The title compound exists as a purple solid and was isolated as the major product from the reaction between Prdpa and copper(II) nitrate in methanol, using either a 1:1, or 2:1, ligand to metal ratio. Crystals suitable for X-ray crystallographic studies were obtained by slow recrystallisation from MeOH. It was found that in the solid state the title compound crystallised in the $P2_1/a$ space group. The monoclinic unit cell (a = 8.850 Å, b = 15.609 Å, c = 9.923 Å, $\alpha = \gamma = 90°$, $\beta = 97.357(2)°$) is composed of a mononuclear, neutral

$[Cu(Prdpa)_2(NO_3)_2]$ molecule containing a six-co-ordinate copper centre with an axially distorted octahedral geometry, Figure 4.3

The central copper atom occupies a centre of symmetry with the two bidentate Prdpa ligands occupying the equatorial plane [Cu-N6,N6' = 1.993(6) Å; Cu-N2,N2' = 2.010(5) Å], whilst the two monodentate nitrate groups occupy the axial positions [Cu-O2,O2' = 2.509(3) Å]. The pyridyl rings are considered to be planar and the dihedral angle formed between the two planes is 128.4°. Unlike $[Cu(Hdpa)(NO_3)_2]$ there is no secondary amine moiety in $[Cu(Prdpa)_2(NO_3)_2]$ that can participate in hydrogen bonding. However there is a short contact, of 2.47 Å, between the proton on C(12) and the O-atom of a co-ordinated nitrate group. The other bond lengths and angles in the primary co-ordination sphere of the central copper atom are recorded in Table 4.1. Selected crystallographic data for the title compound are presented in ***Appendix A***.

Atoms	Distance / Å
Cu-N(6) / Cu-N(6)'	1.993(6)
Cu-N(2) / Cu-N(2)'	2.010(5)
Cu-O(2) / Cu-O(2)'	2.509(3)
	Angle / °
N(6)-Cu-N(2) / N(6)'-Cu-N(2)'	86.07(5)
N(6)'-Cu-N(2) / N(6)-Cu-N(2)'	93.93(5)
C(5)-N5-C(7) / C(5)'-N(5)'-C(7)'	119.20(1)
N(6)-Cu-O(2) / N(6)'-Cu-O(2)'	82.12(3)
N(2)-Cu-O(2) / N(2)'-Cu-O(2)'	85.35(3)

Table 4.1. Bond lengths and angles in the primary co-ordination sphere of 34.

4.0.1.1.2 The Crystal Structure of [Cu(Prdpa)(NO$_3$)$_2$], 35

The title complex exists as a green solid and was isolated as the minor product from the reaction between copper(II) nitrate and Prdpa in methanol, or as the only product when the reaction is carried out in acetone. Crystals suitable for X-ray crystallographic studies were obtained by slow recrystallisation from CH_2Cl_2/cyclohexane. In the solid state the title compound crystallises in the $P2_1/n$ space group. The monoclinic unit cell (a = 8.297 Å, b = 13.214 Å, c= 18.057 Å, $\alpha = \gamma = 90°$, $\beta = 101.917°$) is composed of a mononuclear, neutral [Cu(Prdpa)$(NO_3)_2$] molecule with a five-co-ordinate copper centre exhibiting a distorted square pyramidal geometry, Figure 4.4.

The bidentate Prdpa ligand lies in the equatorial plane [Cu-N1 = 1.961(2) Å; Cu-N2 = 1.981(2) Å], as do the two monodentate nitrate groups [Cu-O1 = 1.966(2) Å; Cu-O4 = 2.010(2) Å]. An oxygen atom from a nitrate group in another unit cell co-ordinates to the copper centre in the axial position [Cu-O6#1 = 2.408(2) Å], thus producing a pseudo-polymeric lattice structure, Figure 4.5. The pyridyl rings are considered to be planar and the dihedral angle formed between the two planes is 146.1°. Other relevant bond lengths and angles in the primary co-ordination sphere of the central copper atom are recorded in Table 4.2. Selected crystallographic data for this compound are presented in ***Appendix B***.

Atoms	Distance / Å
Cu-N1	1.961(2)
Cu-N2	1.981(2)
Cu-O1	1.966(2)
Cu-O4	2.010(2)
Cu-O6#1	2.408(2)
	Angle / °
N1-Cu-O1	176.64(8)
N1-Cu-N2	87.15(8)
O1-Cu-N2	93.21(8)
N1-Cu-O4	91.87(7)
O1-Cu-O4	88.53(7)
N2-Cu-O4	167.14(7)
N1-Cu-O6#1	92.54(7)
O1-Cu-O6#1	84.30(8)
N2-Cu-O6#1	115.86(7)
O4-Cu-O6#1	76.99(7)

Table 4.2. Bond distances and angles in the primary co-ordination sphere of 35

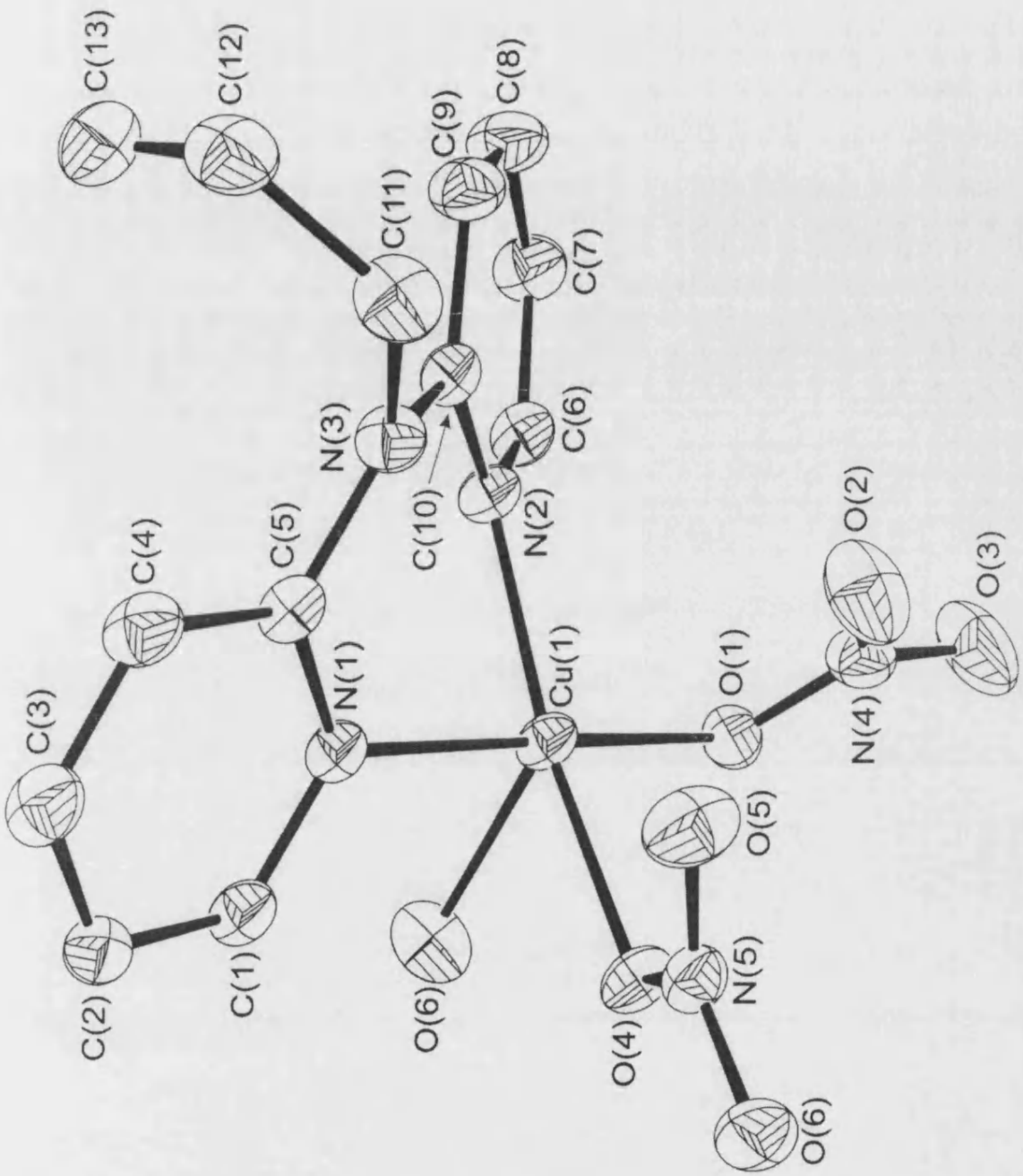


Figure 4.4. Molecular structure of 35.

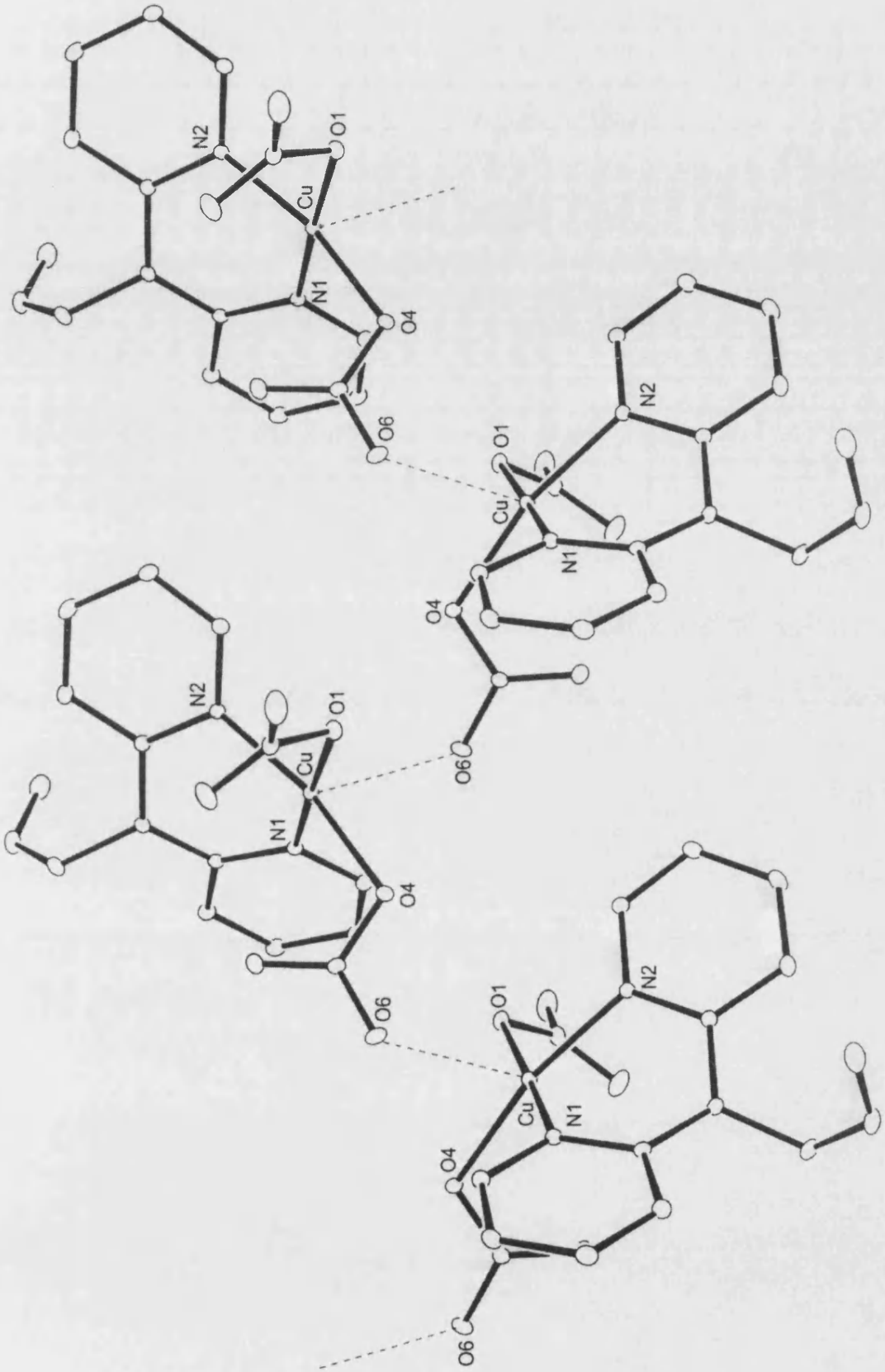


Figure 4.5. Extended lattice structure of 35.

4.0.1.1.3 The Crystal Structure of [Cu(Hdpa)(NO$_3$)$_2$], 36

This green complex resulted from the reaction described previously between copper(II) nitrate and Hdpa[2] in either acetone or MeOH. Crystals suitable for X-ray crystallographic studies were obtained by slow evaporation of solvent from a methanolic solution of [Cu(Hdpa)(NO$_3$)$_2$]. It was found that in the solid state the title compound crystallised in the Pc2$_1$b space group. The orthorhombic unit cell (a = 9.6630 Å, b = 13.3680 Å, c= 20.3340 Å, $\alpha = \beta = \gamma = 90°$) is composed of two, mononuclear, neutral [Cu(Hdpa)(NO$_3$)$_2$] molecules, both of which contain an axially distorted octahedral geometry around copper, Figure 4.6.

Each of the [Cu(Hdpa)(NO$_3$)$_2$] molecules in the unit cell have the same binding motif, but slightly different geometries. Both units contain one bidentate Hdpa ligand [Cu(1)-N(1) = 1.956(5) Å; Cu(1)-N(2) = 1.945(5) Å; Cu(2)-N(6) = 1.939(5) Å; Cu(2)-N(7) = 2.002(4) Å], and one chelating nitrate ligand [Cu(1)-O(1) = 2.043(5) Å; Cu(1)-O(2) = 2.021(4) Å; Cu(1)-O(7) = 2.002(4) Å; Cu(1)-O(8) = 2.073(5) Å] occupying the equatorial plane. The second nitrate group bridges between the copper and the metal in an adjacent unit cell, thus extending the structure into a linear polymer, Figure 4.7. The two polymeric strands are also linked *via* hydrogen bonds between the central N-H moiety of the Hdpa ligand, on one strand, and the two oxygen atoms of the bridging nitrate ligand on the other [H(3)-O(10) = 2.97(4) Å; H(3)-O(12) = 3.13(1) Å; H(8)-O(6) = 2.94(8) Å; H(8)-O(4) = 3.10(0) Å]. The two pyridyl rings in the ligand are approximately planar with a dihedral angle of 167.8° between them. Other relevant bond lengths and bond angles in the primary co-ordination sphere of the central copper atoms are recorded in Table 4.3. Selected crystallographic data for the title compound are presented in ***Appendix C***.

Atoms	Distance / Å
Cu(1)-N(1)	1.956(5)
Cu(1)-N(2)	1.954(5)
Cu(1)-O(1)	2.043(5)
Cu(1)-O(2)	2.021(4)
Cu(1)-O(4)	2.335(5)
Cu(1)-O(6)'	2.434(6)
Cu(2)-N(6)	1.944(5)
Cu(2)-N(7)	1.939(5)
Cu(2)-O(7)	2.002(4)
Cu(2)-O(8)	2.073(5)
Cu-O(10)	2.332(6)
Cu-O(12)"	2.448(6)
	Angle / °
N(1)-Cu(1)-N(2)	95.4(2)
N(6)-Cu(2)-N(7)	95.94(2)
O(1)-Cu(1)-O(2)	64.5(2)
O(7)-Cu(2)-O(8)	63.7(2)
O(4)-Cu(1)-O(6)'	166.8(2)
O(10)-Cu(2)-O(12)"	171.7(2)
O(4)-Cu(1)-O(1)	81.5(2)
O(4)-Cu(1)-O(2)	79.8(2)
O(4)-Cu(1)-N(1)	102.7(3)
O(4)-Cu(1)-N(2)	96.3(3)
O(10)-Cu(2)-O(7)	92.5(3)
O(10)-Cu(2)-O(8)	94.3(2)
O(10)-Cu(2)-N(6)	105.2(3)
O(10)-Cu(2)-N(7)	83.3(3)
C(5)-N(3)-C(6)	133.8(5)
C(15)-N(8)-C(16)	131.9(5)

Table 4.3. Bond lengths and angles in the primary co-ordination sphere of 36.

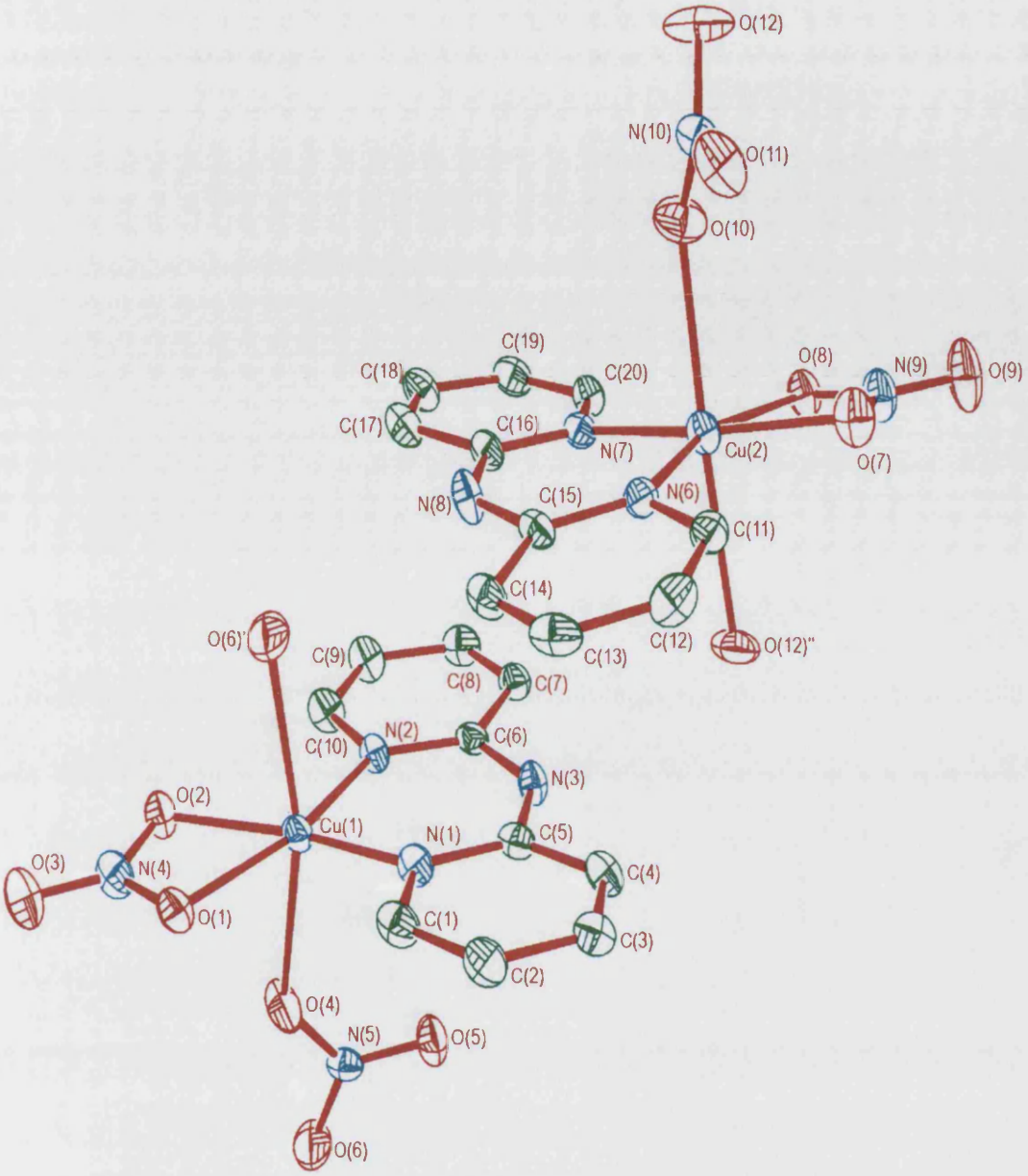


Figure 4.6. Unit cell structure of 36.

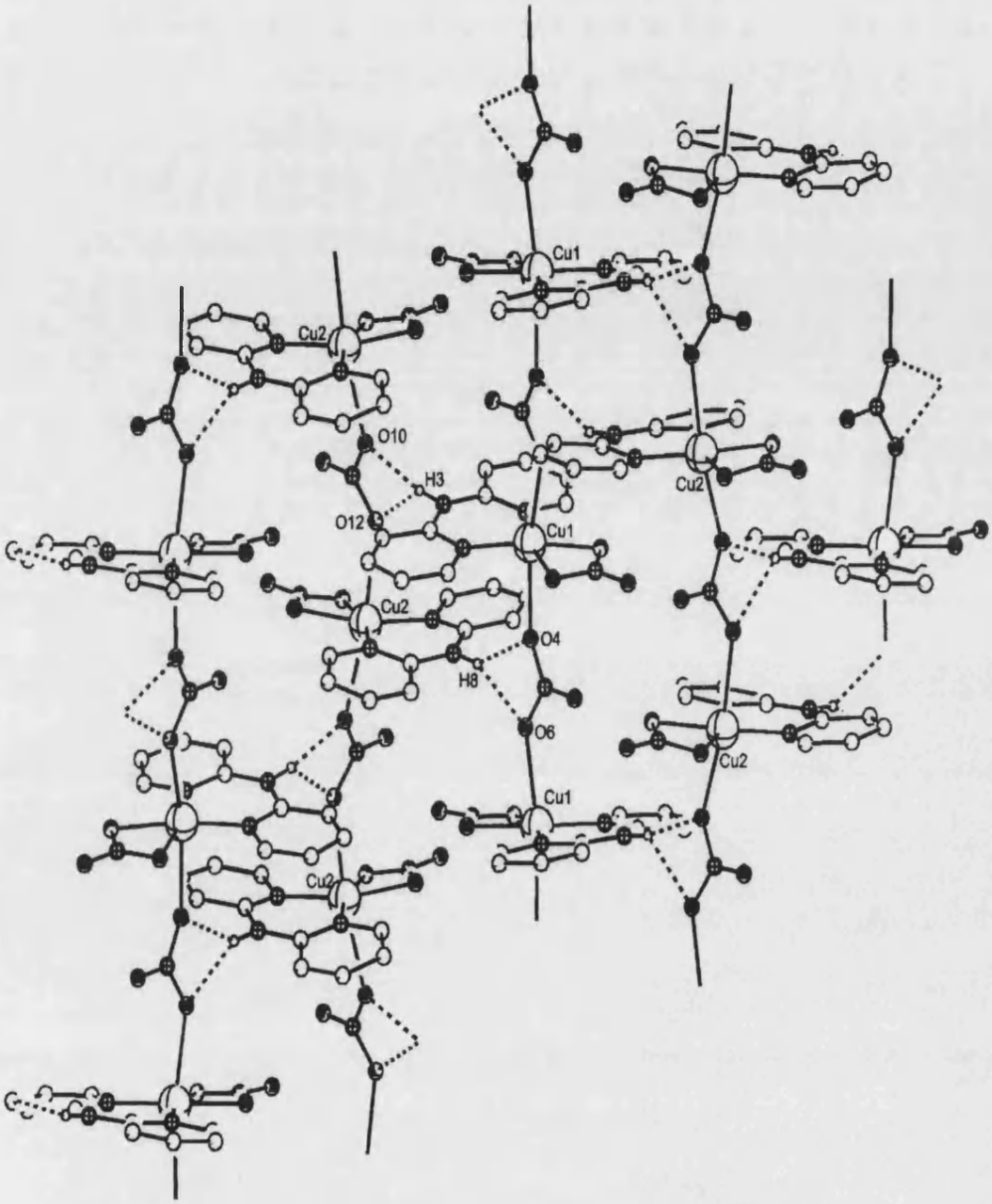


Figure 4.7. Extended lattice structure of 36.

4.1.1.2 Copper(II) Chloride

The reaction between copper(II) chloride and Prdpa was carried out in methanol under the same conditions used for preparing $Cu(NO_3)_2$ complexes. The light green product, isolated in 90% yield, was identified as the 1:1 adduct $[Cu(Prdpa)Cl_2]$, **37**, Scheme 4.6.

$$\text{Prdpa} + CuCl_2 \xrightarrow[RT]{MeOH} [Cu(Prdpa)Cl_2]$$

Scheme 4.6. Synthesis of 37.

This compound has been reported previously but not structurally characterised[5]. The analogous 1:1 complex formed by the reaction between $CuCl_2$ and Hdpa has also been reported.[6] Crystallography revealed that the structure of $[Cu(Hdpa)Cl_2]$[7] is similar to that of the analogous dibromide complex which contains a compressed tetrahedral geometry about copper as shown in Figure 4.8.[8] It seems likely that **37** also has a similar co-ordination geometry to its Hdpa-CuX_2 analogues. Although two 2:1 Hdpa-$CuCl_2$ adducts $[Cu(Hdpa)_2Cl]Cl$[9] and $[Cu(Hdpa)_2Cl)]Cl \cdot H_2O$,[10] have been isolated, and adducts of the general formula $[Cu(Hdpa)_nX_2]$ (where n = 1 or 2) are now known for all the halides X, except for X = F,[11] there was no evidence from these investigations for the formation of the corresponding 2:1 Prdpa-$CuCl_2$ adduct.

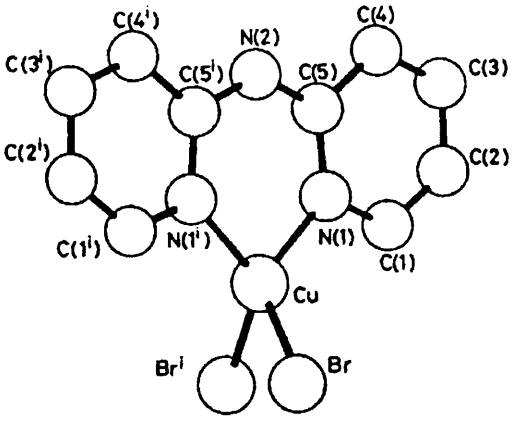


Figure 4.8. Molecular structure of $[Cu(Hdpa)Br_2]$. Error! Bookmark not defined.

4.1.1.3 Zinc(II) Chloride

The zinc(II) analogues of the copper(II) complexes described above were also prepared in order to investigate their solution spectroscopic properties using NMR.

The reaction between Prdpa and zinc(II) chloride gave white crystals of $[Zn(Prdpa)Cl_2]$, **38**, in good yields (86%), Scheme 4.7. The proton and carbon resonances of Prdpa (Tables 4.4 and 4.5 respectively) showed distinct shifts on co-ordination to Zn. Given the 1:1 stoichiometry observed and the d^{10} configuration of Zn(II), it is very likely that the central zinc atom exhibits a tetrahedral geometry, as is commonly found for $[Zn(bidentate)Cl_2]$ complexes.[12]

$$\text{Prdpa} + ZnCl_2 \xrightarrow[RT]{MeOH} [Zn(Prdpa)Cl_2]$$

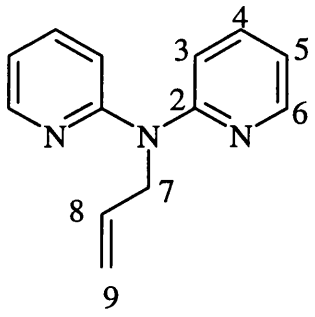
Scheme 4.7. Synthesis of 38.

4.1.1.4 Zinc(II) Nitrate

The analogous reaction between Prdpa and $Zn(NO_3)_2 \cdot 3H_2O$ gave white crystals of $[Zn(Prdpa)(NO_3)_2]$, **39**, in high isolated yields (73%), Scheme 4.8. Both ^1H (see Table 4.4) and ^{13}C (see Table 4.5) NMR data revealed changes in the chemical shifts of the aromatic and alkenyl substituent resonances on complexation of the ligand.

$$Zn(NO_3)_2 + \text{Prdpa} \xrightarrow[RT]{MeOH} [Zn(Prdpa)(NO_3)_2]$$

Scheme 4.8. Synthesis of 39.



Proton	δ_{Prdpa} (ppm)	$\delta_{[Zn(Prdpa)Cl_2]}$ (ppm)	$\delta_{[Zn(Prdpa)(NO_3)_2]}$ (ppm)
H^3	7.16	7.32	7.32
H^4	7.52	7.97	7.99
H^5	6.85	7.32	7.32
H^6	8.33	8.55	8.49
H^7	4.86	4.65	4.64
H^8	6.02	5.97	5.88
H^9	5. 40, 5.42	5.42, 5.44	5.38, 5.42

Table 4.4. Comparison of ^{1}H NMR data for complexed Prdpa and the free ligand. Data recorded in$CDCl_3$.

Carbon	δ_{Prdpa} (ppm)	$\delta_{[Zn(Prdpa)Cl_2]}$ (ppm)	$\delta_{[Zn(Prdpa)(NO_3)_2]}$ (ppm)
C^2	157.1	155.4	156.0
C^3	137.2	141.6	142.0
C^4	114.5	116.9	117.1
C^5	117.0	120.6	120.7
C^6	148.2	147.0	147.3
C^7	50.3	54.8	55.6
C^8	134.7	131.8	131.5
C^9	115.7	120.2	120.4

Table 4.5. Comparison of ^{13}C NMR data for complexed and free Prdpa. Data recorded in $CDCl_3$.

In the ^{1}H NMR spectrum of both **38** and **39**, the pyridyl ring protons all appear at a higher chemical shift than the corresponding signals for the free ligand. A comparison of the ^{13}C NMR spectra shows that three of the five carbons in the pyridyl ring also have a higher chemical shift on complexation, whereas the two carbons that are α to the co-ordinating *N*-

atom (C^2 and C^6) both have slightly lower chemical shifts. The resonances corresponding to the CH group of the *N*-alkenyl substituent in both the ^1H and ^{13}C NMR spectra of both **38** and **39**, appear at a lower chemical shift than in the free ligand. This implies that this methyne group is not as acidic as that in **34,** in which a C-H--O hydrogen bond is observed (**Section 4.0.1.1.1**).

The IR spectrum of **39** shows absorbances at 1008 (ν_{sym}), 1271 and 1491 cm^{-1}(ν_{asym}) typical of a bidentate nitrato ligand, indicating that an octahedral Zn complex is probably formed. This was confirmed when the structure of **39** was determined.[13] The molecular unit consists of a central zinc atom co-ordinated by two, chelating, unsymmetrically bound nitrato groups, and one bidentate 2,2'-dipyridylamine moiety, generating a highly distorted octahedral geometry, Figure 4.9.[13] We are unaware of any literature report for the crystal structure of the Hdpa analogue.

Selected bond lengths and angles for **39** are presented in Table 4.6 below. The deviation of the bond lengths and angles around the metal atom provide an indication as to the degree of distortion from a regular octahedral geometry. Four of the six bond lengths in the primary co-ordination sphere fall within the range of 2.069 ± 0.03 Å; the remaining two Zn-O bonds are much longer (2.279 and 2.350 Å). Of the angles formed in the primary co-ordination sphere only three are approximately 90°, with the remaining three at least 10° greater than this value.

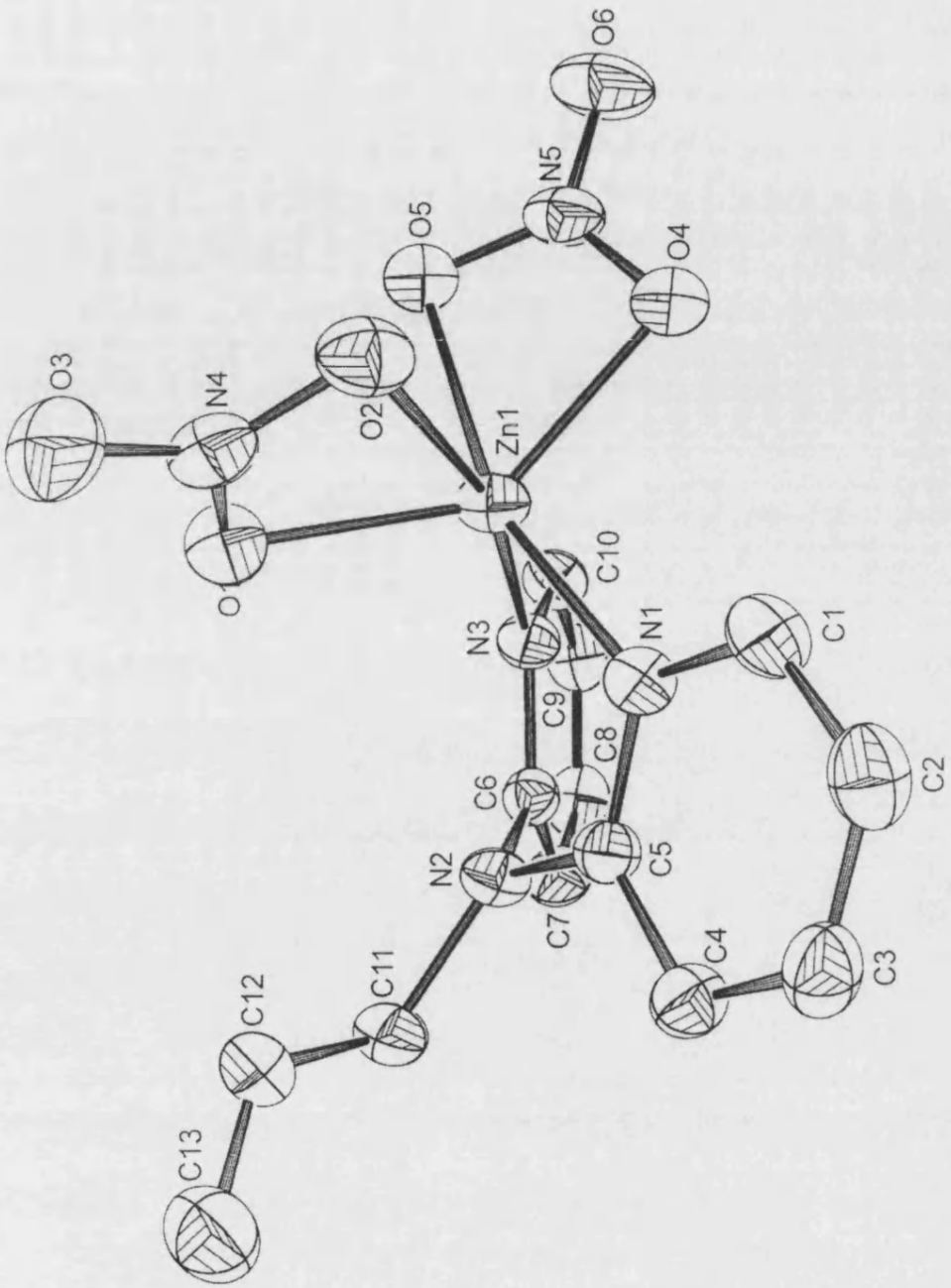


Figure 4.9. Unit cell structure of 39[13].

Atoms	Bond distances / Å
Zn(1)-N(1)	2.043(2)
Zn(1)-N(3)	2.039(2)
Zn(1)-O(1)	2.055(2)
Zn(1)-O(2)	2.350(3)
Zn(1)-O(4)	2.099(2)
Zn(1)-O(5)	2.279(3)
	Bond Angle / °
N(3)-Zn(1)-O(1)	107.50(10)
N(1)-Zn(1)-O(1)	101.63(10)
N(1)-Zn(1)-O(2)	90.85(9)
N(3)-Zn(1)-O(2)	97.16(10)
N(1)-Zn(1)-O(4)	103.55(10)
N(3)-Zn(1)-O(4)	105.47(10)
N(1)-Zn(1)-N(3)	89.43(10)

Table 4.6. Selected bond lengths and angles of 39.

Although $Zn(BF_4)_2$ reacts with just over a two-fold excess of Hdpa in refluxing methanol to afford a 2:1 Hdpa:Zn complex,[14] our attempts to prepare a 2:1 Prdpa/$Zn(NO_3)_2$ complex in either cold or refluxing methanol failed. In both cases only the 1:1 complex was isolated (Scheme 4.9). As expected the direct addition of excess Prdpa to $[Zn(Prdpa)(NO_3)_2]$ also failed to yield the 2:1, complex. Unlike $Cu(NO_3)_2$, $Zn(NO_3)_2$ forms only a 1:1 adduct with Prdpa in methanol, but as noted previously the structures of these two analogues are very different.

$$2.1\ \text{Rdpa} + ZnX_2 \xrightarrow[T]{\text{MeOH}} [Zn(\text{Rdpa})_nX_2]$$

R = H, X = BF_4, T = 65°C, n = 2
R = Propenyl, X = NO_3, T = RT or 65°C, n = 1

Scheme 4.9. Reactions of Zn(II) salts with Rdpa.

4.1.2 2,2'-Dipyridyl(N-pentenyl)amine, Pedpa

The ligand 2,2'-dipyridyl(*N*-pentenyl)amine, Pedpa, is a higher homologue of the previously reported Prdpa, which after attachment to a siloxyl chain provides a product with a longer spacer chain between the *N*-donor centre and the model or polymer backbone. It was not anticipated that its reactions with Cu(II) salts would be significantly different then those of Prdpa but its reaction in a 1:1 molar ration with $Cu(NO_3)_2$ was investigated to confirm this. It was found that, on refrigeration, a mixture of purple and blue solids precipitated from a methanolic solution after addition of a small quantity of diethylether to the reaction mixture. Both solids were isolated by filtration and separated by their differing solubilities. The blue solid was soluble in CH_2Cl_2 and could be recovered unchanged from that solvent, whereas the purple compound was essentially insoluble in all common organic solvents. The microanalytical results identified the blue complex as the 1:1 adduct $[Cu(Pedpa)(NO_3)_2]$, **40**, (yield = 39%), and the purple complex as the 2:1 adduct $[Cu(Pedpa)_2(NO_3)_2]$, **41**, (yield = 7%), Scheme 4.10. Apart from the ratio of the yields, the result is analogous to that found for Prdpa.

$$3\ \text{Pedpa} + 2\ Cu(NO_3)_2 \xrightarrow[RT]{MeOH} [Cu(Pedpa)(NO_3)_2] + [Cu(Pedpa)_2(NO_3)_2]$$

Scheme 4.10 Synthesis of 40 and 41.

Although crystals of a high enough quality to allow the structures of **40** and **41** to be determined by X-ray crystallography could not be grown, structural predictions were made from their infrared spectra. By correlating the nitrato binding modes, as determined by crystallography, of complexes **33, 34, 35** and **36** with their solid state IR spectra, these compounds were used as models which allowed the nitrate co-ordination modes in **40** and **41** to be inferred from their IR spectra.

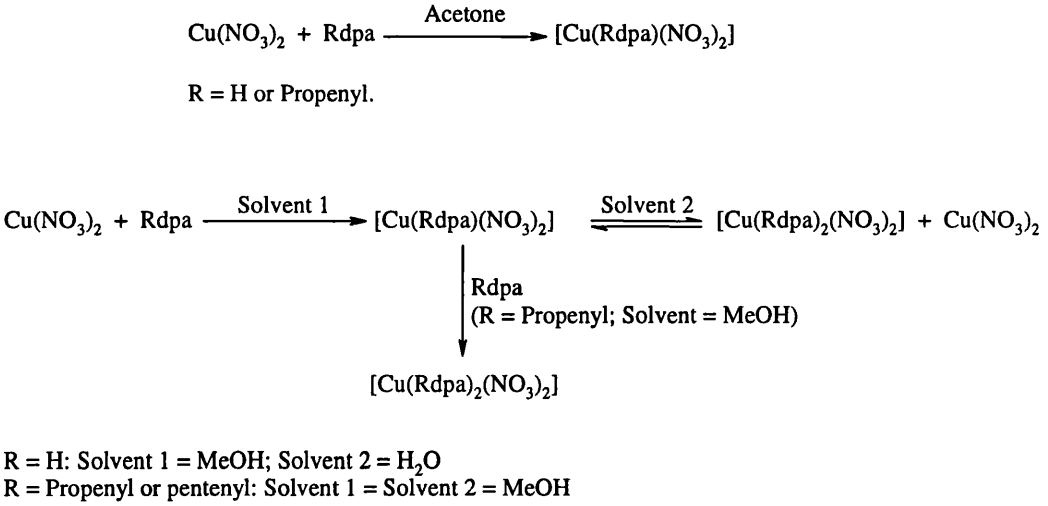
The IR spectrum of **40** has absorbances at 1024,1293 and 1460 cm^{-1}, which are assigned as the symmetric and two asymmetric stretches of the nitrato ligands. These data indicate that the ligand binds to the Cu(II) centre in a monodentate fashion, as they appear at similar wave numbers to those found in **33** (1019, 1269 and 1468 cm^{-1}) and **34** (1026 1268 and

1471 cm^{-1}). As complexes **33, 34** and **40** all have a ligand to metal ratio of 2:1, it is likely that all three exhibit the same basic co-ordination geometry about the Cu(II) centre.

IR absorbances assigned to the nitrato ligand in **41** appear at 1029, 1285 and 1460 cm^{-1}, which again is indicative of the ligand binding in a monodentate fashion. These values are quite different from those found for the 1:1 ($Cu(NO_3)_2$:Rdpa) complexes **35** (1008, 1271 and 1491 cm^{-1}) and **36** (1014, 1251, and 1465 cm^{-1}). The former contains bridging nitrato ligands, and the latter contains asymmetric bidentate nitrates. However, as the highly asymmetric bidentate mode approximates to that of the monodentate, IR data cannot be used unequivocally in this case to infer the nitrato co-ordination mode/s in **41**.

4.1.3 Summary of Complex Formation between Rdpa and $Cu(NO_3)_2$

The reaction between Hdpa and $Cu(NO_3)_2$ in acetone affords the 1:1 complex, **36**, which precipitates as it is insoluble in the solvent. This compound disproportionates on treatment with water and the 2:1 adduct **33** is formed. This pattern of reactivity is mirrored by the reaction of Prdpa with copper(II) nitrate in acetone, which yields exclusively **35**. In methanol the initial green solution containing **35**, slowly precipitates the purple 2:1 adduct **34** on standing, indicating that the 1:1 adduct containing Prdpa also disproportionates in polar solvents. The reaction can be driven in favour of **34** by adding excess ligand to **35** in methanol. Scheme 4.11 summarises these observations.



Scheme 4.11. Summary of reactions between $Cu(NO_3)_2$ and Rdpa.

4.1.4 Structural Comparisons Between Cu-Rdpa Complexes

Complexes formed between copper(II) and Rdpa have been shown to take up a variety of co-ordination geometries ranging from tetrahedral, $[Cu(Hdpa)Br_2]$,**Error! Bookmark not defined.** square pyramidal, $[Cu(Prdpa)(NO_3)_2]$, (see Section **4.0.1.1.2**) and octahedral, $[Cu(Hdpa)_2(NO_3)_2]$.[3] The conversion from a secondary to a tertiary acyclic amine functionality on *N*-alkenylation of Hdpa has the potential to effect the co-ordination geometry of any complexes formed, which in turn could affect any catalytic activity shown by the complex. Thus *N*-alkenylated Rdpa is a better model for siloxane-supported Rdpa then Hdpa itself. Therefore the structures of the three Cu-Prdpa complexes reported here, have been compared with those of relevant Cu-Hdpa complexes.

Presented in Table 4.7 are selected crystallographic data from this work and from other investigations into the co-ordination chemistry of Hdpa towards Cu(II). Although the contents of Table 4.7 are not exhaustive, they allow some significant conclusions to be reached. For compounds of the formula $[Cu(Hdpa)_nX_2]$, where n = 1 and X is a monodentate anion, distorted tetrahedral geometries are frequently observed. This is also the case when n = 2 and X is a non-co-ordinating anion. For complexes with n = 2 in which X is monodentate, then an octahedral geometry is favoured. An octahedral or distorted square-based geometry is observed when n = 1 and X can exhibit either bi- or mono-dentate binding modes

The N-Cu-N bite angle formed by the two co-ordinated, pyridyl nitrogens of Hdpa or Rdpa and the central copper atom all fall within the range of $95 \pm 10°$, indicating that there is some flexibility inherent in both ligands. The Cu-N bond lengths in Table 4.7 fall within the narrow range of 1.986 ± 0.178 Å. As these bond lengths are very similar, it appears that *N*-alkylation does not seriously affect the nature of the $N_{pyridyl}$-Cu bond.

Direct comparison of octahedral $[Cu(Hdpa)_2(NO_3)_2]$ and $[Cu(Prdpa)_2(NO_3)_2]$ shows that whilst both have very similar Cu-N bond lengths, N-Cu-N bite angles as well as $C\text{-}N_{exocylic}\text{-}C$ bond angles, there are also two major differences:

- The dihedral angles formed between the planes of the pyridyl rings are significantly different. For the Hdpa adduct the angle is 37.4° whilst in the alkenylated analogue it is 51.6°.
- Although both compounds exhibit hydrogen-bonding interactions they differ very significantly. In $[Cu(Hdpa)_2(NO_3)_2]$ there is an intermolecular hydrogen-bond linking the N-H amine moiety of co-ordinated Hdpa with a nitrato ligand of a molecule in an adjacent unit cell, so extending the structure into a pseudo-polymer (Figure 4.7). However, $[Cu(Prdpa)_2(NO_3)_2]$ has an intramolecular hydrogen-bonding interaction between the nitrato ligand and the methyne C-H of the propenyl chain. This indicates that there is an increase in the acidity of this proton due to its proximity to the tertiary amine moiety of the ligand. However a similar interaction was not found in the corresponding 1:1 adduct, $[Cu(Prdpa)(NO_3)_2]$, possibly due to the difference in co-ordination geometry, and hence the proximity of the *N*-alkenyl substituent to a nitrato group.

A comparison of the two compounds $[Cu(Prdpa)(NO_3)_2]$ and $[Cu(Hdpa)(NO_3)_2]$ is also revealing.

- There is a change in co-ordination geometry from octahedral ($[Cu(Hdpa)(NO_3)_2]$) to square pyramidal ($[Cu(Prdpa)(NO_3)_2]$).
- The dihedral angles found in the two complexes are markedly different; 25.6° in the Hdpa adduct and 54.7° in the Prdpa adduct.
- Both exhibit pseudo-polymeric structures *via* a bridging nitrato ligand.
- The N-Cu bond lengths and N-Cu-N bond angles are similar.

There are also three Cu(II)-Hdpa adducts in Table 4.7 that contain two crystallographically inequivalent metal-ligand molecules in the unit cell. In $[Cu(Hdpa)(NO_3)_2]$ the metal centres have nearly identical geometries (page 124) and exhibit NH--ON hydrogen-bonding. In $[Cu(CH_3COO)(Hdpa)(ONO)]$,[4] which also contains two molecules in the unit cell, two distorted CuO_4N_2 octahedra are linked together by $O_{acetato}$-$CH_{pyridyl}$ hydrogen bonds. These molecules are in turn linked by NH--ON hydrogen-bonds to another pair of molecules in the adjacent unit cell, so producing an overall tetrameric structure. Only in

Complex	Cu Co-ordination Geometry	Dihedral Angle / °	C-$N_{exocyclic}$-C / °	Cu-N / Å	N-Cu-N / °	Ref.
$[Cu(dpa)_2]$	Tetrahedral	—	127.9	1.952(2) 1.955(2)	101.42(12) 100.67(13)	15
$[Cu(Hdpa)(NO_3)_2]$	Octahedral / Octahedral	12.2	133.8 131.9	1.956(5) 1.954(5)	95.4(2) 95.94(2)	Section **4.0.1.1.3**
$[Cu(Hdpa)_2(NO_3)_2]$	Octahedral	37.4	122.9	2.012(2) 2.007(2)	85.52(8)	3
$[Cu(CH_3COO)(Hdpa)(ONO)]$	Octahedral / Octahedral	—	132.7(2) 131.7(2)	1.975(2) 1.979(2) 1.979(2) 1.965(2)	93.2(1) 92.5(1)	4
$[Cu(Hdpa)_2Br_2].2H_2O$	Octahedral	39.4	117.5	2.029(5) 1.984(5)	85.4(2)	11
$[Cu(Hdpa)Br_2]$	Tetrahedral	7.0	—	1.96(3)	94.8(15)	**Error! Bookmark not defined.**
$[Cu(Hdpa)_2][BF_4]_2$	Tetrahedral	9.9 10.8	93.3 95.4	1.945(5) 1.967(5)	93.3(2) 95.4(2)	16
$[Cu(Hdpa)_2(SCN)_2]$	Octahedral	40.0	125.0	2.022(3) 2.015(4)	85.7(1) 101.1(1)	3 (i)
$[Cu(Hdpa)_2(NCS)]$ (ClO_4)	Square Pyramidal	21.9 32.3	126.8 131.0	2.014(4) 2.016(4) 2.002(4) 2.139(4)	87.9(1) 88.1(1)	3 (i)
$[Cu_2(Hdpa)(OH)_2(BF_4)_2]$	Square Pyramidal	6.59	132.9(3)	1.977(3) 1.977(3)	92.7(1)	17
$[Cu(Hdpa)_2(CH_3CO_2)_2].H_2O$	Square Pyramidal	25.3	—	1.971(8) 2.000(8)	92.0(3)	3 (ii)
$[Cu(Hdpa)(NO_3)Cl].0.5\ H_2O$	Square Pyramidal	30.4	127.5(2)	1.974(2) 2.007(2)	88.8(1)	18
$[Cu(Hdpa)_2(CH_3CO_2)]NO_3$	Octahedral	27.9 27.4	127.1(6) 127.6(6)	2.011(5) 2.037(6) 2.007(6) 2.162(6)	87.5(2) 88.3(2)	19
$[Cu(Hdpa)_2(CHO_2)]BF_4$	Octahedral	26.7 23.6	127.2(7) 129.4(8)	1.999(7) 2.021(7) 2.015(7) 2.164(7)	88.1(3) 89.2(3)	19
$[Cu(Prdpa)_2(NO_3)_2]$	Octahedral	51.6	119.2	2.010(5) 1.993(6)	86.07(5)	Section **4.0.1.1.1**
$[Cu(Prdpa)(NO_3)_2]$	Square Pyramidal	54.7	124.1	1.981(2) 1.961(2)	87.15(8)	Section **4.0.1.1.2**
$[Cu(Hdpa)(NO_2)_2]$	Octahedral	25.6	—	1.966(1) 1.986(1)	92.14(5)	20

Table 4.7. Selected crystallographic data for Cu-Rdpa complexes.

$[Cu(Hdpa)_2(NCS)_{1.5}(ClO_4)_{0.5}]^3$ are there two separate co-ordination geometries present in the molecular species in the unit cell. The first has the formula $[Cu(Hdpa)_2(SCN)_2]$ and is a centrosymmetric octahedron, with two Hdpa ligands co-ordinating equatorially, and two elongated, axial bonds to the SCN^- ligands, and the second is a five-co-ordinate, cationic species $[Cu(Hdpa)_2(NCS)]^+$ with a distorted square pyramidal geometry. Thus it is rare, but not unknown, for two Cu(II)-Hdpa complexes with very different co-ordination geometries to exist in the same unit cell.

In summary the most significant differences between *N*-alkenylated Rdpa- and Hdpa-Cu(II) complexes are:

- There is a considerable increase in the dihedral angle between the pyridine rings of the ligand on *N*-alkenylation. The dihedral angle between pyridyl rings in Cu(II) complexes of Hdpa falls in the range 9 - 42°.[21] In both the Cu(II)-Prdpa complexes with crystal structures reported herein the corresponding dihedral angles are greater than the highest end of the range found for the Hdpa analogues.
- *N*-alkenylation of Hdpa is sufficient to change the primary co-ordination sphere around Cu(II) (*cf.* $[Cu(Hdpa)(NO_3)_2]$ compared to $[Cu(Prdpa)(NO_3)_2]$).
- Intermolecular NH--anion hydrogen-bonding interactions are prevalent in Hdpa complexes. *N*-alkenylation prevents NH--anion hydrogen-bonding but facilitates CH-oxoanion hydrogen-bonding and hence alters the intramolecular forces which determine long range molecular interactions.

4.1.5 Bis-2-methylpyridyl(N-propenyl)amine, Prbmpa, Adduct

The 1:1 adduct of $Cu(NO_3)_2$ with Prbmpa was synthesised in ethanol and precipitated as a dark blue solid. Complex **42** was recrystallised from CH_2Cl_2/cyclohexane in 74% yield, Scheme 4.12, and identified as $[Cu(Prbmpa)(NO_3)_2]$ by microanalysis. The IR spectrum of **42** showed absorbances at 1028, 1279 and 1456 cm^{-1} which indicates that the complex contains monodentate nitrato groups. The ligand could not be attached to a siloxane, and no attempt was made to obtain X-ray quality crystals of this compound.

$$Cu(NO_3)_2 + \text{Prbmpa} \xrightarrow[RT]{EtOH} [Cu(\text{Prbmpa})(NO_3)_2]$$

Scheme 4.12. Synthesis of 42.

It is worth noting that the unsubstituted analogue of Prbmpa, bis-2-methylpyridylamine (Hbmpa) readily behaves as a facially co-ordinating, tridentate ligand, and the crystal structure of $[Cu(Hbmpa)(NO_3)_2]$ has been determined.[22] The metal exhibits a distorted, five-co-ordinate geometry, that is intermediate between a square-based pyramid and a trigonal bipyramid arrangement, Figure 4.1. If regarded as trigonal bipyramidal, the two pyridyl nitrogens occupy the axial positions whilst the amine moiety and the two monodentate nitrato groups are in the equatorial plane.

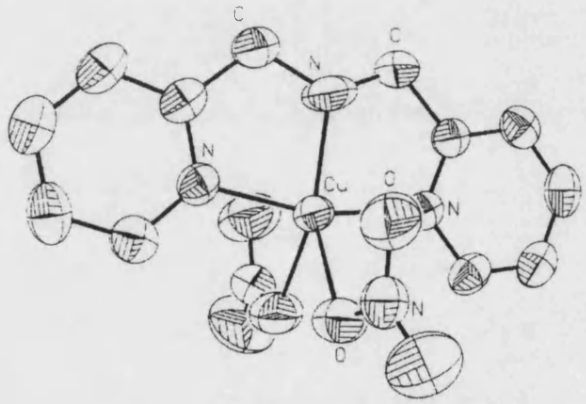


Figure 4.10. Molecular structure of $[Cu(Hbmpa)(NO_3)_2]$.[22]

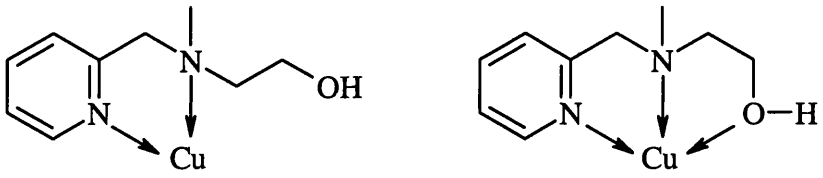
4.1.6 2-Methylamino(N-methyl-N-2-hydroxyethyl)pyridine, Mamp, Adduct

On reacting $CuCl_2$ with Mamp in a 1:1 stoichiometry in ethanol at room temperature, a pale blue solid precipitated. Pure $[Cu(MampCl_2]$, **43**, was isolated in 40% yield after recrystallisation from CH_2Cl_2/cyclohexane, Scheme 4.13.

$$CuCl_2 + \text{Mamp} \xrightarrow[RT]{EtOH} [Cu(\text{Mamp})Cl_2]$$

Scheme 4.13. Synthesis of 43.

Although Mamp has been synthesised previously[23] a search of the literature has failed to reveal any reference to its use as a ligand. It is possible that it could behave as either a bidentate or tridentate ligand, as illustrated in Scheme 4.14. As Mamp could not be attached to a siloxane backbone, and has not featured in catalytic studies, this compound was not characterised in detail.



Scheme 4.14. Bi- and tridentate co-ordination modes of Mamp.

4.2 Complexes of Cyclic *N*-Donor Ligands

The ability of copper, and other metallic complexes containing the aza-macrocyclic ligand, triazacyclononane, H_3tacn, to bind dioxygen has been well-documented (see **Chapter 1**). It was hoped that by functionalising the three secondary amine moities of the ligand, it would be possible to bind it to an organosiloxane, as shown in **Chapter 3**, and after metallation, create siloxane supported precursors for the catalytic deactivation of chemical agents. Reported below are details of the metallated complexes of 1,4,7-tri-(*N*-propenyl) and 1,4,7-tri-(*N*-pentenyl)-triazacyclononane that were synthesised and characterised in this study.

4.2.1 1,4,7-Tri(N-propenyl)-1,4,7-triazacyclononane, Pr_3tacn

4.2.1.1 Copper(II) Nitrate Adduct

The $Cu(NO_3)_2$ complex of Pr_3tacn was synthesised by stirring the reactants together in an alcoholic solution, Scheme 4.15. The crude product formed after 1 hour was purified by

recrystallisation from CH_2Cl_2/cyclohexane, to afford $[Cu(Pr_3tacn)(NO_3)_2]$, **44**, as a dark blue solid in 54% yield.

$$Cu(NO_3)_2 + Pr_3tacn \xrightarrow[RT]{EtOH} [Cu(Pr_3tacn)(NO_3)_2]$$

Scheme 4.15. Synthesis of 44.

Crystals of sufficient quality to allow the determination of the structure of **44** were grown from an ethanol/diethyl ether solvent system. The crystal structure of $[Cu(H_3tacn)(NO_3)]$ has not been reported as far as we are aware, but the structure of the close analogue $[Cu(TCD)(NO_3)](NO_3)$ (TCD = 1,4,7-triazacyclododecane), has been determined.[24] This complex is ionic and contains a five-co-ordinate cationic copper centre, and a nitrate counter ion. The metal co-ordination sphere is comprised of the facially co-ordinating TCD ligand and a chelating, bidentate nitrate, Figure 4.11.

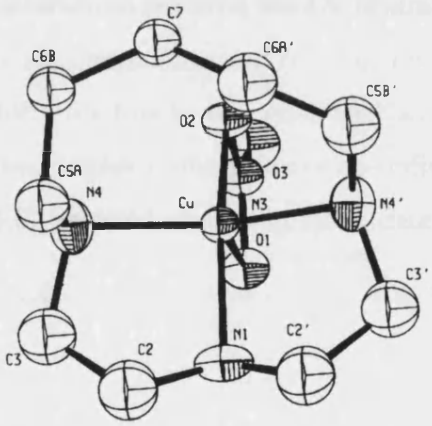


Figure 4.11. Unit cell structure of $[Cu(TCD)(NO_3)](NO_3)$]. Error! Bookmark not defined.

There has been one report in the literature of Pr_3tacn being used as a ligand.[25] Reaction of CuI with Pr_3tacn and CO_2 in the presence of $NaBPh_4$, yielded the complex $[(Pr_3tacn)Cu(\mu\text{-}C_2O_4)Cu(Pr_3tacn)][BPh_4]_2$ after aerial oxidation. The cyclic ligand binds facially to each Cu centre with an oxalate ligand bridging the two metal atoms. The Cu-N bond lengths for this molecule are a little shorter than those found in **44** (see **Section 4.0.1.1.4**) (for

[(Pr_3tacn)Cu(μ-C_2O_4)Cu(Pr_3tacn)]: Cu-N_{ax} = 2.162(5) Å, Cu-N_{eq} = 2.008(4) and 2.016(4) Å; for [Cu(Pr_3tacn)(NO_3)$_2$]: Cu-N_{ax} = 2.228(7) Å; Cu-N_{eq} = 2.063(9) and 2.071(3) Å]).

4.0.1.1.4 The Crystal Structure of [Cu(Pr_3tacn)(NO_3)$_2$], 44

Crystals of the title complex suitable for X-ray crystallographic studies were obtained by slow recrystallisation from CH_2Cl_2/cyclohexane. In the solid state [Cu(Pr_3tacn)(NO_3)$_2$] crystallises in the $P2_1/c$ space group. The monoclinic unit cell (a = 8.297 Å, b = 13.214 Å, c = 18.057 Å, $\alpha = \gamma = 90°$, $\beta = 101.917°$) is composed of a mononuclear, neutral [Cu(Pr_3tacn)(NO_3)$_2$] molecule, containing a five-co-ordinate copper centre exhibiting a distorted square pyramidal geometry, Figure 4.12. The tridentate Pr_3tacn ligand occupies two equatorial and one axial position with two monodentate nitrate groups occupying the other equatorial positions. The axial Cu-N bond length is much longer than the two equatorial Cu-N bond lengths [Cu-N1 = 2.228(7) Å; Cu-N2 = 2.063(9) Å; Cu(1)-N(3) = 2.071(3) Å], whilst the two Cu-O separations are comparable [Cu-O1 = 1.973(0) Å; Cu-O4 = 1.994(9) Å]. A very weak interaction between the Cu centre and a second oxygen from one of the nitrato groups has also been observed (Cu-O(3) = 2.711(2) Å). However, the inter-atomic distance is too long for this to be considered as a true bonding interaction. Other relevant bond lengths and angles in the primary co-ordination sphere of the copper atom are recorded in Table 4.8. Selected crystallographic data for the title compound are presented in ***Appendix D.***

Atoms	Distance / Å
Cu(1)-O(1)	1.9730(16)
Cu(1)-O(4)	1.9949(16)
Cu(1)-O(3)	2.711(2)
Cu(1)-N(1)	2.2287(18)
Cu(1)-N(2)	2.0639(18)
	Angle / °
O(1)-Cu(1)-O(4)	97.68(7)
O(4)-Cu(1)-O(3)	77.87(7)
O(1)-Cu(1)-O(3)	52.17(6)
O(4)-Cu(1)-N(1)	96.26(7)
O(4)-Cu(1)-N(2)	85.34(7)
O(4)-Cu(1)-N(3)	170.81(7)
O(1)-Cu(1)-N(1)	107.91(7)
O(1)-Cu(1)-N(2)	167.27(7)
O(1)-Cu(1)-N(3)	90.79(7)
N(1)-Cu(1)-N(2)	83.93(7)
N(2)-Cu(1)-N(3)	85.63(7)
N(3)-Cu(1)-N(1)	84.44(7)
N(1)-Cu(1)-O(3)	157.17(6)
N(2)-Cu(1)-O(3)	117.10(6)
N(3)-Cu(1)-O(3)	104.88(7)
Cu(1)-N(1)-C(1)	112.60(13)
Cu(1)-N(2)-C(6)	114.51(14)
Cu(1)-N(3)-C(11)	113.10(13)

Table 4.8. Bond lengths and angles in the primary co-ordination sphere of 44.

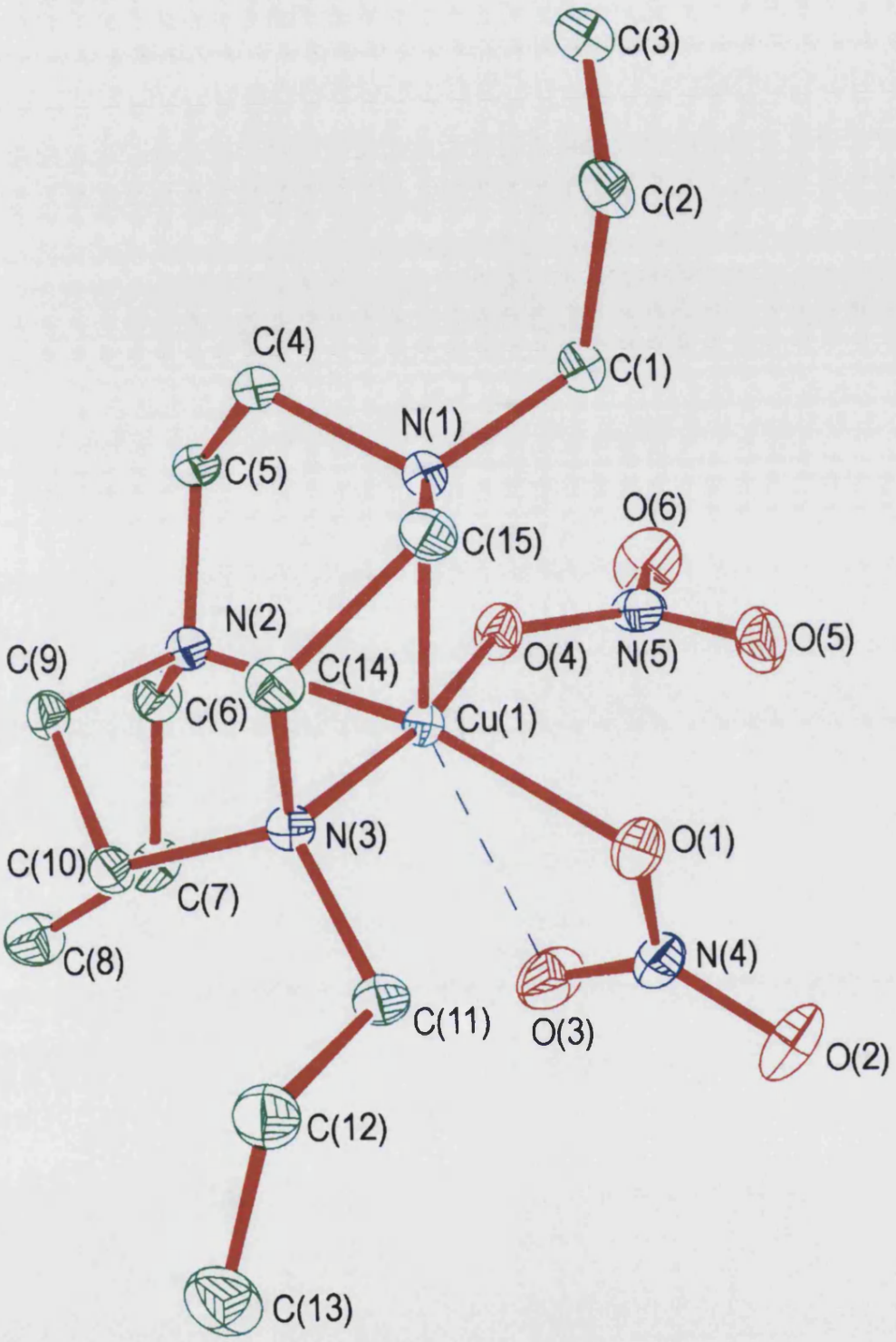


Figure 4.12. Molecular structure of 44.

4.2.1.2 Zinc(II) Nitrate Adduct

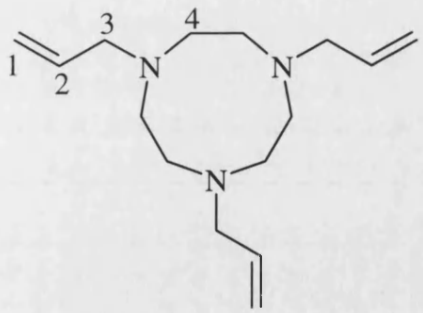
The analogous reaction between $Zn(NO_3)_2$ and Pe_3tacn was investigated to probe any changes in the ^1H and ^{13}C NMR spectra of the ligand on complexation. An analogous procedure to that given above yielded the white complex $[Zn(Pr_3tacn)(NO_3)_2]$, **45**, in moderate yields (34%), Scheme 4.16

$$Zn(NO_3)_2 + Pr_3tacn \xrightarrow[RT]{EtOH} [Zn(Pr_3tacn)(NO_3)_2]$$

Scheme 4.16. Synthesis of 45.

The complex formed between H_3tacn and $Zn(NO_3)_2$ has been synthesised previously and used to investigate the catalytic transesterification and hydrolysis of RNA,[1] but no crystal structure has so far been reported. It is known that that R_3tacn will bind in a tridentate fashion to the metal centre, and from the IR spectrum a prediction can be made as to the binding mode of the nitrato ligands by comparison with compound **44**. For **44** the IR absorbances assigned to the monodentate nitrates appear at 1019, 1293 and 1461 cm^{-1} whilst in the IR spectrum of **45** the nitrato absorbances were assigned as 1037, 1289 and 1456 cm^{-1}. These data are sufficiently similar to indicate that both **45** and **44** contain monodentate nitrato ligands and 5-co-ordinate metal centres.

The ^1H data for **45** (Table 4.9) show that the complexed and free ligands have quite different proton chemical shifts. Protons in the alkenyl chains increase their chemical shifts slightly on complexation, but maintain their splitting patterns. Both the chemical shifts and splitting pattern of the protons of the macrocyclic ring change significantly on complexation. Ring protons resonate as a singlet at $\delta = 2.75$ ppm in the free ligand and as two broad multiplets of equal intensities which are centred at $\delta = 2.92$ ppm in **45**, Figure 4.13. This coupling pattern is indicative of an AA'BB' spin system arising from the magnetic inequivalence of the macrocyclic protons after complexation. Hagen *et al.* observed a similar pattern in the ^1H NMR spectrum of $[Zn(^iPr_3tacn)](ClO_4)_2]$ ($^iPr_3tacn$ = 1,4,7-tri(isopropyl)-1,4,7-triazacyclononane).[26]



Proton	δ_{Pr_3tacn} (ppm)	$\delta_{[Zn(Pr_3tacn)(NO_3)_2]}$ (ppm)
H^1	5.89 (ddt)	5.97 (ddt)
H^2	5.01, 5.05 (2 x dd)	5.36, 5.39 (2x dd)
H^3	3.14 (d)	3.55 (d)
H^4	2.75 (s)	2.92 (m)

Table 4.9. Comparison of ^{1}H NMR data for complexed Pr_3tacn and the free ligand. Multiplicities are in parentheses. Data recorded in $CDCl_3$.

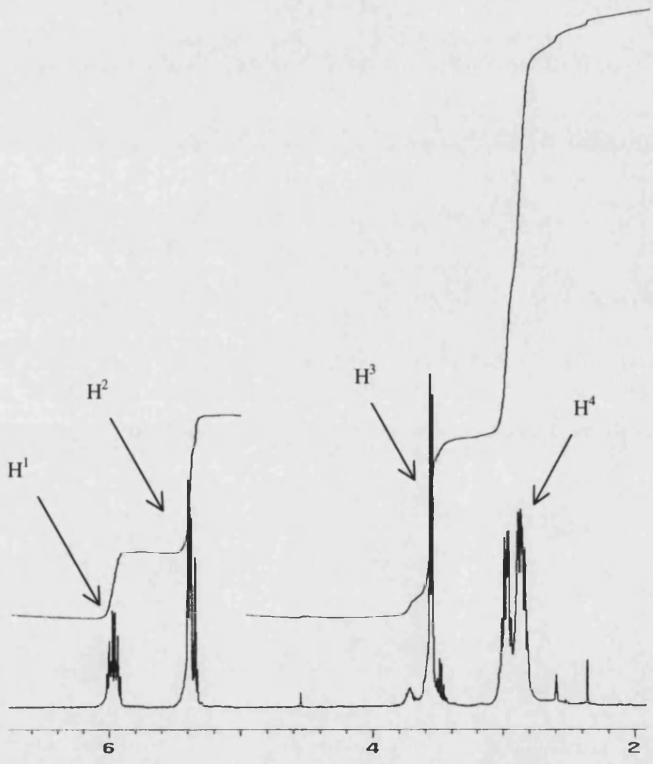


Figure 4.13. ^{1}H NMR spectrum of 45.

The ^{13}C NMR data for the complexed and uncomplexed ligand (Table 4.10) also show slight differences in chemical shift for analogous carbon atoms.

Carbon	δ_{Pr_3tacn} (ppm)	$\delta_{[Zn(Pr_3tacn)(NO_3)_2]}$ (ppm)
C^1	116.4	122.9
C^2	136.8	130.0
C^3	61.9	60.3
C^4	55.3	49.8

Table 4.10. Comparison of ^{13}C NMR data for complexed Pr_3tacn and the free ligand. Data recorded in $CDCl_3$.

4.2.2 1,4,7-Tri(N-pentenyl)-1,4,7-triazacyclononane, Pe_3tacn

The room temperature reaction of copper(II) nitrate with Pe_3tacn in ethanol led to the precipitation of light blue crystals of [1,4,7-tri(N-pentenyl)triaza-cyclononane]copper(II) nitrate, $[Cu(Pe_3tacn)(NO_3)_2]$, **46**, in moderate yields (50%), Scheme 4.17.

$$Cu(NO_3)_2 + Pe_3tacn \xrightarrow[RT]{EtOH} [Cu(Pe_3tacn)(NO_3)_2]$$

Scheme 4.17. Synthesis of 46.

Attempts to grow crystals of high enough quality for a structure to be determined failed. From the IR spectrum of **46** the absorptions assigned to the nitrato ligands appear at 1022, 1286 and 1461 cm^{-1} which are very similar to the values found for **44** (1019, 1293 and 1461 cm^{-1}). Therefore it seems likely that in the solid state this complex will adopt a similar structure to that of **44** (see page 143). The IR spectrum of **46** also shows an absorption at 1642 cm^{-1} assigned to the terminal alkene functionality. In the free ligand the C=C absorption occurs at 1640 cm^{-1}, indicating that the pendant arms, as expected, do not bind to the copper(II) centre.

4.2.3 Structural comparison of $[Cu(Pr_3tacn)(NO_3)_2]$ with other Cu-R_3tacn Complexes

The co-ordination chemistry of R_3tacn has been the subject of three reviews in the last fifteen years. The first concerned itself solely with the chemistry of the unsubstituted ligand (R = H)[27] whilst the other two reviewed the metal complexes formed with R_3tacn bearing *N*-alkyl or aryl substituents.[28,29] Whilst there is a pronounced tendency for unsubstituted and mono-*N*-substituted ligands to form both 1:1 complexes, $[LM^{n+}X_n]$[30] and 2:1 complexes, $[L_2M^{n+}X_n]$[30,31] (where M= metal, L = H_3tacn or RH_2tacn) the more highly substituted ligands R_2Htacn, R_3tacn and R_2R'tacn favour 1:1 adduct formation.[32,33,34] H_3Tacn derivatives containing one or more substituents also increase the likelihood of binuclear species being formed, which has made the ligand particularly attractive for modelling the active centre of enzymes for purposes of catalysis (see **Chapter 1**).[35]

A majority of crystallographically characterised copper(II) complexes containing a H_3tacn derivative with the general formula $LCuX_2$ are five co-ordinate, with the copper exhibiting a distorted square pyramidal geometry (the crystal structure of **44** presented in **Section 4.0.1.1.4** is a good example of this). In the presence of non-co-ordinating counter ions such as X= $[ClO_4]^-$ or $[PF_6]^-$, complexes of the type $[CuL_2]X_2$ are generally formed.[36] Because both tridentate macrocyclic ligands bind facially to the metal centre, a distorted octahedral geometry is exclusively observed.[37]

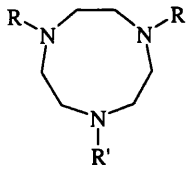
Whilst a detailed comparison of the 5- and 6-co-ordinate species cannot be made directly, there are some general features that are common to both. Table 4.11 details the Cu-N axial and equatorial bond lengths, as well as the N_{eq}-Cu-N_{eq} bond angles, for a selection of 5-and 6-co-ordinate mononuclear Cu-R_3tacn complexes. Surprisingly few structures of mono-nuclear Cu(II)-R_3tacn adducts have been reported.

The compound $[(Pr_3tacn)Cu(C_2O_4)Cu(Pr_3tacn)]$ is included in Table 4.11 as it is the only Cu(II)-Pr_3tacn adduct known prior to this investigation, and so a comparison can be drawn with the structure of **44**.

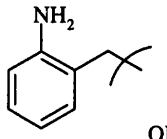
Complex	Cu Co-ordination Geometry	Cu-N_{eq} / Å	Cu-N_{ax} / Å	N_{eq}-Cu-N_{eq} / °	Reference
$[Cu(Pr_3tacn)(NO_3)_2]$	Square Pyramidal	2.063(9) 2.071(3)	2.228(7)	85.63(7)	Section **0**
$[Cu(H_3tacn)Cl_2]$	Square Pyramidal	2.063(4) 2.038(4)	2.246(4)	82.2(2)	38
$[Cu(H_3tacn)Br_2]$	Square Pyramidal	2.046(4) 2.047(4)	2.230(4)	82.32(17)	39
$[Cu(H_3tacn)_2](ClO_4)_2$	Octahedral	2.087(6) 2.176(6)	2.233(7)	81.97(25)	37
$[Cu(pptacn)Cl_2]$	Square Pyramidal	2.115(1) 2.090(1)	2.228(1)	85.08(5)	40
$[Cu(PeyneH_2tacn)_2]Cl_2$	Octahedral	2.026(5) 2.045(5)	2.256(4)	81.7(2)	36
$[Cu(ByneH_2tacn)_2](PF_6)_2$	Octahedral	2.065(2) 2.018(2)	2.541(2)	83.23(9)	36
$[Cu(BuH_2tacn)_2](BPh_4)$	Octahedral	2.020(8) 2.043(8)	2.527(9)	82.7(5)	32
$[Cu(H_3tacn)_2][Cu(CN)_3]$	Octahedral	2.048(2) 2.077(2) 2.063(2) 2.058(2)	2.305(2) 2.336(2)	83.6(1) 82.9(1)	41
$[Cu(TCTA)]^{\cdot}$	Octahedral	2.197(3) 2.039(2)	2.115(3)	82.8(1)	42
$[Cu(AB_3tacn)](ClO_4)_2$	Square Pyramidal	2.041(9) 2.073(9)	2.268(10)	85.7(4)	43
$[Cu(Phen_3tacn)]$	Square Pyramidal	2.083(3) 2.039(3)	2.320(3)	85.4(1)	44
$[Cu(daptacn)](ClO_4)_2$	Square Pyramidal	2.080(13) 2.061(12)	2.251(12)	86.3(5)	45
$[Cu(Me_3tacn)(N_3)_2)$	Square Pyramidal	2.035(2) 2.072(2)	2.238(2)	82.7(1)	46
$[(Pr_3tacn)Cu(C_2O_4)Cu(Pr_3tacn)]$	Square Pyramidal	2.008(4) 2.016(6)	2.162(5)	87.2(1)	25

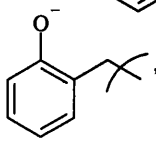
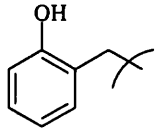
Table 4.11. Crystal Structure data for a range of Cu-R_3tacn adducts.

Key for Table 4.11:



[Cu(Pptacn)Cl_2] - R = R' = 5-phenyl-4-pentenyl.
[Cu($PeyneH_2$tacn)Cl_2] - R = H, R' = pentynyl.
[Cu($ByneH_2$tacn)]$(PF_6)_2$ - R = H, R' = butynyl.
[Cu(BuH_2tacn)$_2$]$(BPh_4)_2$ - R = H, R'= butenyl.
[Cu(daptacn)]$(ClO_4)_2$ - R = 3-aminopropyl, R' = H.
[Cu(Me_3tacn)$(N_3)_2$] - R = R' = Methyl
[Cu(TCTA)] - R = R' = CH_2COO^-

[Cu(Ab_3tacn)]$(ClO_4)_2$ - R = R' = 

[Cu($Phen_3$tacn)] - R =  , R' = 

As copper(II) has a d^9 electronic configuration, any complexes that it forms are susceptible to Jahn-Teller distortion effects. This can be most clearly seen in the octahedral complexes where the N_{ax}-Cu bond lengths are significantly longer (~0.2-0.5 Å) than the corresponding N_{eq}-Cu bond lengths. A distorted octahedral geometry is also confirmed by the bond angles formed between the two equatorial N-atoms, with the Cu centre at the vertex which fall in the range 81-83°. Rather similar values are found for the N_{eq}-Cu-N_{eq} in square pyramidal complexes. The [Cu(TCTA)]$^-$ anion contains a CuN_3O_3 core with a prismatic geometry. Although the difference in energy between this and an octahedral arrangement is small, the prismatic geometry is rare and may result from the steric constraints imposed on the metal centre by the ligands three pendant $[CH_2CO_2]^-$ groups.[42]

From the data presented above it can be seen that the complex [Cu(Pr_3tacn)$(NO_3)_2$] is typical of other Cu-R_3tacn complexes in that it has a square pyramidal geometry. The N_{ax}-Cu bond length is longer than the N_{eq}-Cu bond lengths (*cf.* ~2.2 as compared to ~2.0 Å respectively) and the angle formed between the two equatorial nitrogens and the copper centre is ~ 85°. The other known Cu-Pr_3tacn adduct, [(Pr_3tacn)Cu(C_2O_4)Cu(Pr_3tacn)], which also adopts a distorted square pyramidal geometry, has a slightly shorter N_{ax}-Cu separation than [Cu(Pr_3tacn)$(NO_3)_2$], whereas the two N_{eq}-Cu lengths are similar. The N_{eq}-Cu-N_{eq} bond angle for this copper adduct is ~87° which is close to the ideal square

pyramidal value of 90°. In $[Cu(Pr_3tacn)(NO_3)_2]$ the value observed is ~85°. This slight difference can be explained by differences in the nature of the binding modes between the nitrato ligand in $[Cu(Pr_3tacn)(NO_3)_2]$, and the oxalate ligand in $[(Pr_3tacn)Cu(C_2O_4)Cu(Pr_3tacn)]$. In the latter the oxalate forms a strained five-membered ring with each copper centre. In $[Cu(Pr_3tacn)(NO_3)_2]$ the nitrate ligands are monodentate, which does not constrict the geometry as much. However, on consideration of the error limits of each crystal structure it appears that the Cu(II) centres in each structure have virtually identical primary co-ordination sphere geometries.

4.3 Conclusions

An important aspect of this investigation was concerned with the identification and structural characterisation of complexes formed between the functionalised *N*-donor ligands and copper salts in particular. To this end the compounds $[Cu(Prdpa)_2(NO_3)_2]$, $[Cu(Prdpa)(NO_3)_2]$, $[Cu(Prdpa)Cl_2]$, $[Cu(Pedpa)(NO_3)_2]$, $[Cu(Pedpa)_2(NO_3)_2]$, $[Cu(Prbmpa)(NO_3)_2]$, $[Cu(Mamp)Cl_2]$, $[Cu(Pr_3tacn)(NO_3)_2]$ and $[Cu(Pe_3tacn)(NO_3)_2]$ have been synthesised and characterised. For comparative purposes the zinc analogues $[Zn(Prdpa)Cl_2]$, $[Zn(Prdpa)(NO_3)_2]$ and $[Zn(Pr_3tacn)(NO_3)_2]$ were also prepared.

The reaction of either Prdpa or Pedpa with copper(II) nitrate is solvent dependant and capable of affording complexes with both 1:1 and 2:1 ligand to metal ratios; the former disproportionate in protic solvents to yield the latter. The complex $[Cu(Hdpa)(NO_3)_2]$ has also been shown to disproportionate on treatment with water to form $[Cu(Hdpa)_2(NO_3)_2]$. Both $[Zn(Prdpa)Cl_2]$ and $[Zn(Prdpa)(NO_3)_2]$ were synthesised by reacting the respective Zn(II) salts with Prdpa in alcoholic media. There was no evidence for the formation of 2:1 ligand to metal adducts in these reactions.

The crystal structure of $[Cu(Prdpa)_2(NO_3)_2]$ was determined. The unit cell is composed of a mononuclear, neutral $[Cu(Prdpa)_2(NO_3)_2]$ molecule with copper in an axially distorted octahedral ligand environment. The two bidentate Prdpa ligands occupy the equatorial sites whilst monodentate nitrato ligands occupy axial sites. An intermolecular hydrogen-bond occurs between the nitrato ligand and the C-H of the non-co-ordinated propenyl chain.

A crystal structure determination of $[Cu(Prdpa)(NO_3)_2]$ revealed a unit cell composed of a mononuclear, neutral $[Cu(Prdpa)(NO_3)_2]$ molecule in which copper exhibited a distorted square pyramidal geometry. One of the nitrato ligands is monodentate and occupies the axial position of the square based pyramid. The chelating bidentate Prdpa ligand and one bidentate nitrato ligand occupy the equatorial sites. The equatorial nitrato group also bridges a copper centre in an adjacent unit cell thus producing a polymeric lattice structure.

The crystal structure of $[Cu(Hdpa)(NO_3)_2]$ was also determined for comparative purposes. The unit cell is composed of two, mononuclear, neutral $[Cu(Hdpa)(NO_3)_2]$ molecules, both

of which contain an axially distorted six-co-ordinate copper centre. The Hdpa ligand occupies two of the equatorial sites whilst a chelating bidentate nitrato ligand occupies the other two. The axial sites are occupied by nitrate groups which bridge copper atoms in adjacent unit cells, thus generating a linear polymeric structure. The two polymeric strands are also linked *via* hydrogen bonds between the central N-H moiety of each Hdpa ligand, on one strand, and two oxygen atoms of bridging nitrate ligands on another.

Comparisons between the structures of these three compounds, and their analogues containing Hdpa, show that the replacement of the N-H group of Hdpa by a *N*-alkenyl substituent increases the dihedral angles formed between the planes of the two co-ordinated pyridyl rings of the ligand. A change in the co-ordination geometry between $[Cu(Prdpa)(NO_3)_2]$ and $[Cu(Hdpa)(NO_3)_2]$ facilitates C-H--oxoanion hydrogen-bonding at the expense of N-H hydrogen-bonding.

The complexes $[Cu(Prbmpa)(NO_3)_2]$ and $[Cu(Mamp)Cl_2]$ were isolated as blue solids from the reaction between the ligand and the corresponding Cu(II) salt in alcoholic solutions, but their chemistry was not pursued further.

The three R_3tacn derivatives, $[Cu(Pr_3tacn)(NO_3)_2]$ $[Zn(Pe_3tacn)(NO_3)_2]$ and $[Zn(Pr_3tacn)(NO_3)_2]$ were all synthesised in an analogous manner and the crystal structure of $[Cu(Pr_3tacn)(NO_3)_2]$ was determined. Each mononuclear, neutral $[Cu(Pr_3tacn)(NO_3)_2]$ molecule contains a five-co-ordinate copper centre exhibiting a distorted square pyramidal geometry. The tridentate Pr_3tacn ligand binds facially and the primary co-ordination sphere is completed by two monodentate nitrato ligands. The only other reported crystal structure of a compound containing Pr_3tacn as a ligand is $[(Pr_3tacn)Cu(\mu\text{-}C_2O_4)Cu(Pr_3tacn)][BPh_4]_2$. This too has Cu(II) centres with a square pyramidal geometry.

^1H NMR studies on $[Zn(Pr_3tacn)(NO_3)_2]$ revealed the expected changes in the splitting pattern of the macrocyclic methylene protons on complexation, as noted previously for other Zn(II)-R_3tacn complexes.**Error! Bookmark not defined.**

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Chapter 5:

Summary and Further Work.

Chapter 5: Summary and Further Work.

5.0 Introduction 160
5.1 Summary and Implications of the Study 160
5.2 Further Work on Ligand Systems 162
5.2.1 Acyclic *N*-Donor Ligands 162
5.2.2 Cyclic *N*-Donor Ligands 163
5.2.3 Metallation of Ligands 165
5.2.4 Poly(siloxane) Membranes 165
5.3 References 167

5.0 Introduction

In this section the different areas of investigation of this study are discussed in terms of their implications for future work on chemical warfare programmes. Different aims and objectives for each section are included.

5.1 Summary and Implications of the Study

As stated in **Chapter 1** the intention of the project was to help seek an alternative to bleaching agents as a "universal decontaminant" for chemical warfare (CW) agents. The principles behind the investigations undertaken in this study were based on the following observations:

- The most obvious choice of method for the destruction of HD is its oxidation to the corresponding sulfoxide, whilst organophosphate based chemical agents are easily destroyed by hydrolysis. In the case of HD a controlled oxidation to the corresponding sulfoxide must take place with little or no over oxidation to the noxious sulfone derivative.
- Cu(II) and Zn(II) with bi- or tri-dentate *N*-donors are known to be excellent hydrolysis catalysts for organophosphates, whilst Cu(II) with bi- or tri-dentate *N*-donor ligands are known to be potential oxidants, either by "activating" O_2 or performing the oxidation themselves and being aerobically re-oxidised from Cu(I) to Cu(II).
- Poly(siloxanes) can be loaded sequentially with more than one side arm and/or a metal species. This makes it possible to introduce more than one active species at either the molecular level as a catalyst, or as a powdered absorbent/decontaminant. Poly(siloxanes) also exhibit a high oxygen solubility as linear polymers and a high oxygen permeability when cross-linked into membranes. They can also be fabricated as coatings.

Thus it was proposed in this DERA financed programme to develop methods for preparing model, short-chain siloxanes, and finally poly(organosiloxanes), functionalised with suitably modified ligating species. The intention was that organofunctionalised polymers

would then by metallated using metal complexes that show catalytic activity towards either hydrolysis or are able to activate molecular oxygen. The model compounds would be used to aid in the characterisation of the polymeric species, and to define the reaction conditions needed for polymer functionalisation. In an alternative approach siloxane membrane films suitable for use as CW barriers would have finely divided reactive solids incorporated within them directly. The two types of functionalised polymers thus produced would then be made available to the sponsors for testing for their ability to deactivate HD and other chemical warfare agents.

An initial key step in this study involved functionalising the ligands, and a series of bi- and tri-dentate *N*-donor ligands containing either 1-alkenyl substituents or in one case a terminal hydroxyl moiety, were first prepared. Both of these functionalities render the ligands suitable for attachment to an organofunctionalised siloxane containing Si-H units *via* a hydrosilylation or dehydrocoupling reaction. However, only two of these ligands were successfully attached to a model trisiloxane and no investigations into their chemistry on a polymeric siloxane framework were undertaken. This study has instead focussed mainly on the chemistry of the complexes formed between the ligands with Cu(II) and Zn(II) salts. As ligand functionalised siloxanes are invariably non-crystalline, even after metallation, no X-ray crystallographic studies are possible. By structurally characterising representative complexes formed between the *N*-alkenylated ligands and a metal salt, predictions can be made about the co-ordination geometries and possible reactivities of the metals after reaction with ligand-functionalised siloxane analogues.

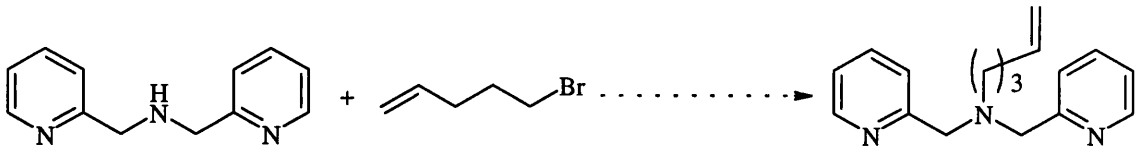
The formation of both 5- and 6-co-ordinate Cu(II) complexes with Rdpa ligands, and the formation of 5-co-ordinate complexes with R_3tacn (where R = propenyl or pentenyl), has implications for the use and possible catalytic activity of siloxane bound species. The hydrolysis of phosphorus-based nerve agents is known to be catalysed by 5-co-ordinate Cu(II)/Rdpa complexes,[1] and phosphate diesters can be catalytically hydrolysed by 5-co-ordinate Cu(II)/H_3tacn complexes.[2] In addition Cu(II)-R_3tacn complexes are known to bind O_2, and Cu(II) itself is a useful oxidant in non-aqueous environments in particular.[3] Therefore, those complexes formed in this study which have yet to be tested should have their catalytic activities compared with those of their non-alkenylated analogues, as we have shown that attaching a side-chain to the ligand does modify both the reactivity, and even the primary co-ordination sphere, of the resulting metal complexes.

The behaviour and stability of polymer and membrane supported species has important ramifications for future applications which need to be considered. We have shown that the copper(II) nitrate complexes formed with Rdpa ligands (where R = H, propenyl or pentenyl) can adopt either 1:1 or 2:1 ligand to metal ratios and that conversion from the 1:1 to 2:1 complexes occurs in aqueous systems with concomitant loss of Cu(II) ions. Thus functionalised siloxane membranes and polymers containing 1:1 Rdpa/Cu(II) sites (where R denotes the siloxane polymer) are expected to be inherently unstable to water and would suffer copper ion leaching. This might be minimised by using metallated materials containing a large excess of ligand sites, which would re-complex any leached metal ions.

5.2 Further Work on Ligand Systems

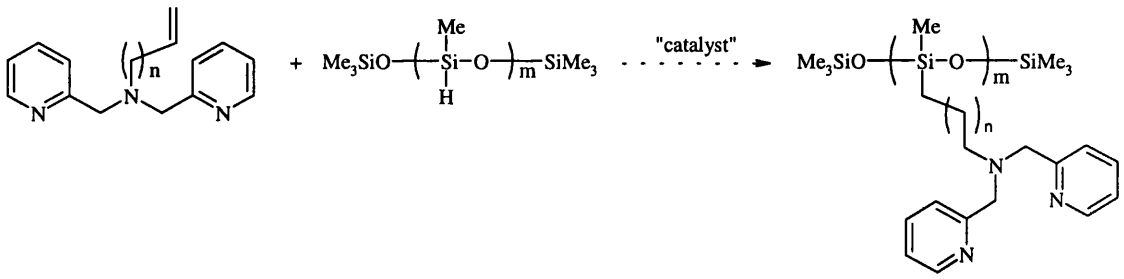
5.2.1 Acyclic N-*Donor Ligands*

The *N*-alkenylated derivatives of Hdpa, Prdpa and Pedpa, were successfully added to a model trisiloxane (see **Chapter 2**). Investigations into acyclic tridentate *N*-donor ligands could be extended by developing a route to the *N*-pentenyl analogue of Prbmpa, Scheme 5.1, so generating a more complete series of pyridyl based functionalised ligands with two different spacer chain lengths and two different denticities for attachment to siloxanes. Tridentate ligands are still viable for catalytic use and are less likely to form metal complexes which disproportionate on contact with the aqueous phase.



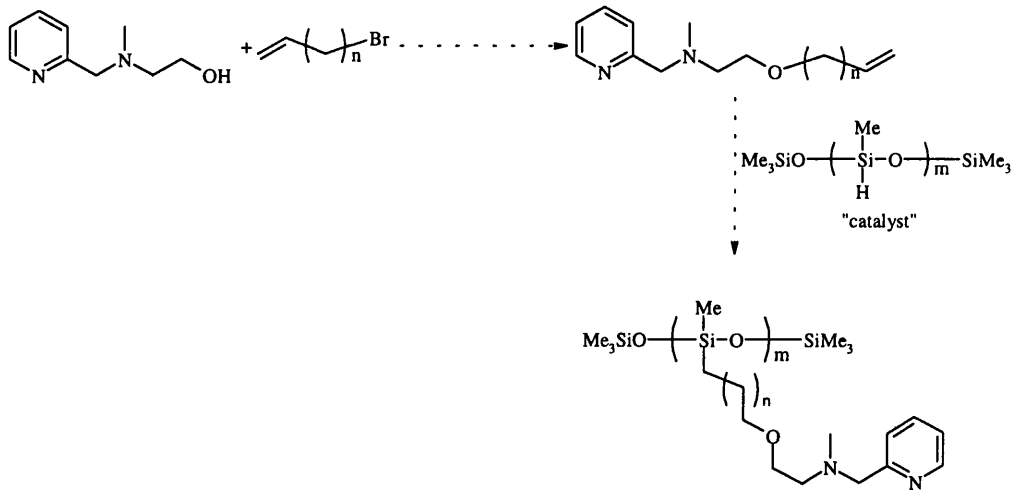
Scheme 5.1. Synthesis of Pebmpa.

The attachment of Prbmpa to Si-H moieties was unsuccessful, possibly because the spacer chain was too short and/or because the ligand interfered with the catalytic cycle of the catalyst. Alternative metal-based or radical catalysts should be screened for their ability to produce modified siloxanes, Scheme 5.2



Scheme 5.2. Synthesis of Rbmpa modified siloxanes.

It was disappointing that the Mamp ligand, which contains a terminal hydroxyl moiety, did not undergo a dehydrocoupling reaction with a trilsiloxane as analogues are known to undergo this reaction.[4] An alternative approach (Scheme 5.3) involving etherification of the hydroxyl moiety to generate a 1-alkenyl species, which should undergo a hydrosilylation reaction, might be explored. Such a procedure would provide a general method for converting ligands with a primary alcohol functionality into materials capable of being hydrosilylated.

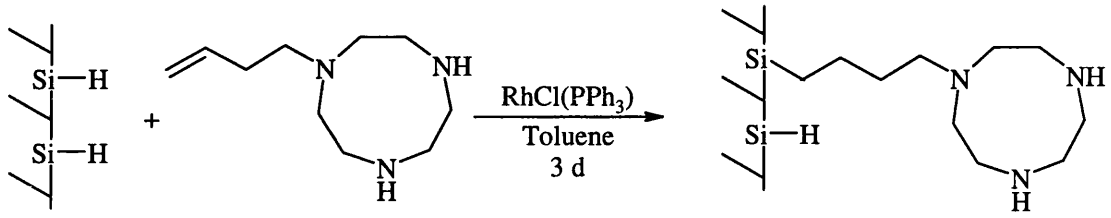


Scheme 5.3. Etherification of Mamp and reaction with a siloxane.

5.2.2 Cyclic N*-Donor Ligands*

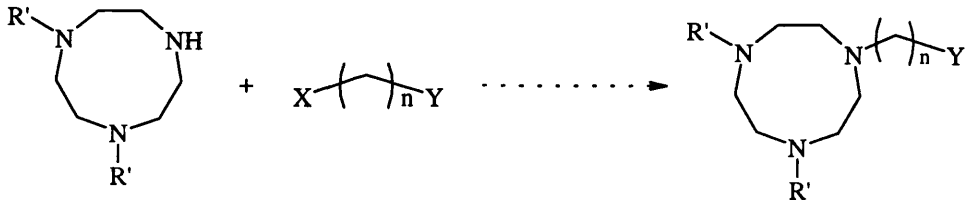
We were unable to hydrosilylate either of the two tri-*N*-alkenyl derivatives of 1,4,7-triazacyclononane, Pr_3tacn and Pe_3tacn, using either platinum catalysed or radical initiated conditions. It has recently been reported that (*N*-butenyl)H_2tacn will undergo

hydrosilylation to a silica surface containing Si-H moieties in the presence of a Rh catalyst, Scheme 5.4.[5] Investigations should be carried out to determine whether the conditions and type of catalyst used for this reaction would also allow Pr_3tacn and Pe_3tacn to be attached to a poly(organosiloxane).



Scheme 5.4. Functionalisation of a silica surface with R_3tacn *via* hydrosilylation.

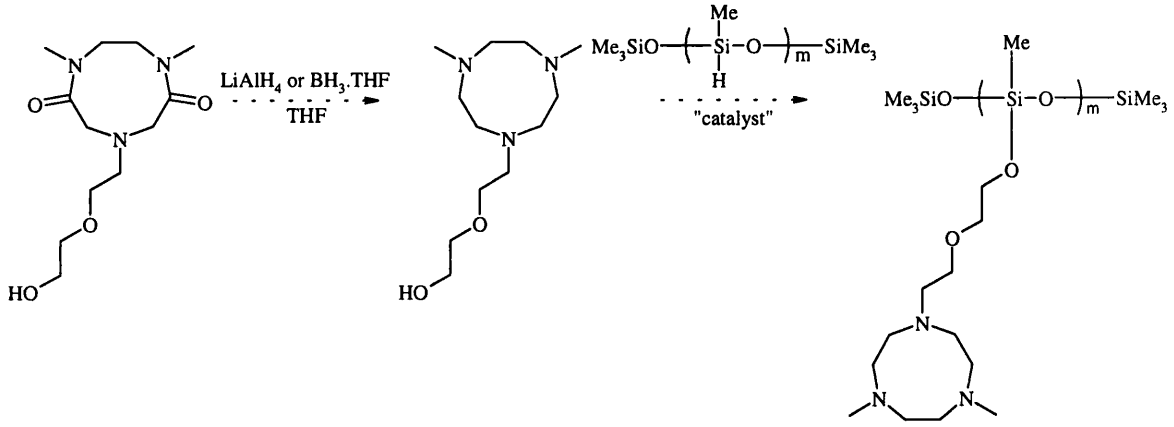
Continued investigations into the synthesis of a mono-substituted R_3tacn unit containing a hydroxyl or alkene terminated chain (Scheme 5.5) would generate a route for the attachment of a triazacyclononane derivative as a side-arm attachment to a siloxane.



X = leaving group such as halides or sulfonate esters;
Y = -OH or -CH=CH_2

Scheme 5.5. Synthesis of R_3tacn containing hydroxyl terminated chains.

Progress was made on the initial steps in the synthesis of such a compound containing a single terminal hydroxyl group, Hedmtacn, but the correct conditions needed for the last step of the synthesis, involving reduction of the amide, were not found. Both $LiAlH_4$ and BH_3·THF have been used by two different research groups, for this or similar transformations,[6,7] and further work is needed to find the exact conditions. If successfully prepared Hedmtacn is also a candidate for a dehydrocoupling reaction, Scheme 5.6, or conversion to a *N*-alkenyl derivative.



Scheme 5.6. Reduction of amide to Hedmtacn and its dehydrocoupling with a model siloxane.

5.2.3 Metallation of Ligands

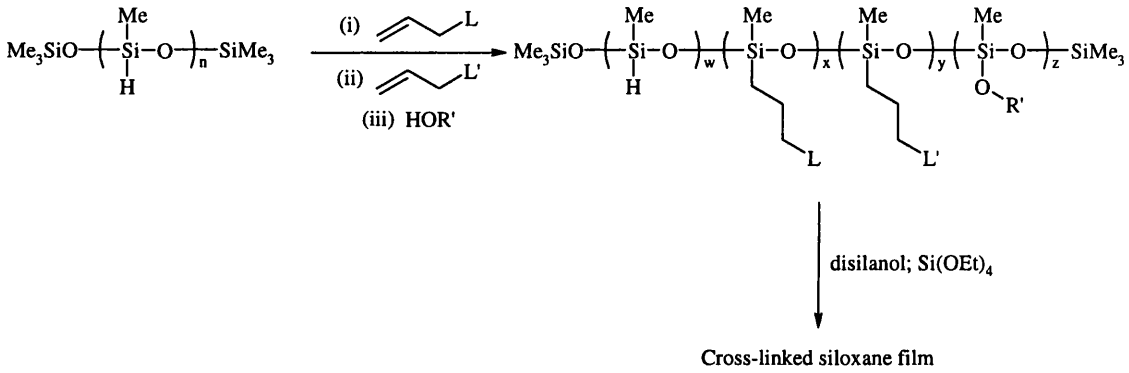
Our investigations of the Rdpa/Cu(II) systems have shown the importance of studying both the solid-state structure and solution behaviour of potentially useful catalysts. This should be continued with the emphasis on metallated acyclic tridentate and cyclic ligands, both in the free state and after attachment to a siloxane backbone. Of particular importance is the stability towards leaching of metallated siloxane materials which show catalytic potential.

This study has been mainly concerned with Cu(II) and Zn(II) salts and their complexes, but complexes of Mn,[8] Co,[9] Ru,[10] Rh[11] and Pt[12] have been reported to possess catalytic activities for reactions relevant to the programme, and these and other transition metals could be complexed with ligands of interest and screened for activity towards CW agents.

5.2.4 Poly(siloxane) Membranes

Investigations in this area can be divided into two. The first is concerned with the preparation and reactivity of metallated organofunctionalised poly(siloxanes) membranes, and the second centres on membranes containing solid species dispersed in them. Although we have successfully demonstrated a procedure for the immobilisation of dispersed metal species in siloxane films, which can be used to prepare reactive membranes with controlled

loadings, we have had very limited success in attaching ligand systems to siloxanes at the molecular level and none at metallating them. This, above all other aspects of these studies, should be pursued. We anticipate that metallation of linear, soluble, ligand-functionalised siloxanes would be readily achieved by reaction with solutions of metal salts, whereas the permeation of metal species into the ligand site of cross-linked films will be a slower, but still realisable, process. The possibility of anchoring more than one catalytically active species on a siloxane, whilst subsequently modifying the properties of the film (e.g. hydrophobic/hydrophilic balance) by reaction with an organic property modifier (Scheme 5.7), has important potential applications in many areas.



Scheme 5.7. Synthesis of a multifunctional cross-linked siloxane film.

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Chapter 6

Experimental

Chapter 6: Experimental

6.0 General Methods. 170
6.0.1 Instrumentation and Solvents. 170
6.0.2 Crystallography 171
6.0.3 Starting Materials. 171
6.1 General Procedures. 172
6.1.1 Organofunctionalisation of Trisiloxanes *via* Hydrosilylation. 172
6.1.2 Membranes Containing Dispersed Solids. 172
6.2 Acyclic *N*-Donor Ligands. 174
6.2.1 Organofunctionalised Trisiloxanes. 177
6.3 Membranes Containing Dispersed Solids 181
6.4 Cyclic *N*-Donor Ligands 181
6.4.1 1,4,7-Triazacyclononane, H_3tacn. 181
6.4.2 Symmetrically Substituted H_3tacn Derivatives. 184
6.4.3 Asymmetrically Substituted H_3tacn Derivatives. 186
6.5 Metal Complexes of *N*-Donor Ligands 187
6.5.1 Complexes of Acyclic *N*-Donor Ligands 187
6.5.1.1 Cu(II) Adducts of Rdpa (R = H or Propenyl) 187
6.5.1.2 Zn(II) Adducts of Rdpa (R = Propenyl) 189
6.5.1.3 Other Cu(II) Adducts 190
6.5.2 Complexes of R_3tacn (R = Propenyl or Pentenyl). 191
6.6 References. 193

6.0 General Methods

6.0.1 Instrumentation and Solvents

NMR data were recorded on either a Jeol GX270 spectrometer (270.05 MHz ^{1}H; 67.8 MHz ^{13}C) or a Jeol EX400 spectrometer (269.55 or 399.65 MHz ^{1}H, 79.3 MHz ^{29}Si; 100.4 MHz ^{13}C). All NMR samples were dissolved in $CDCl_3$ except where stated otherwise. Residual $CHCl_3$ in the solvent was used as an internal standard for ^{1}H (7.27 ppm) and ^{13}C (77.0 ppm) NMR samples which contained Si atoms, and tetramethylsilane was used as an internal standard for samples that did not contain silicon. All chemical shifts are quoted in ppm, and for ^{29}Si NMR samples [$Cr(acac)_3$] was used as a relaxation agent. Infrared spectra were recorded on a Perkin-Elmer 599b spectrometer, either as a liquid film (film) or as a nujol mull (nujol). Elemental analyses were recorded by the Analytical Services Unit, University of Bath. Sonication experiments were performed in the Department using a Sonic Systems P100 sonicator (operating at a nominal frequency of 20 kHz) by kind permission of Dr. G. A. Price.

All solutions were aqueous unless stated otherwise. Solvents for reactions, extractions and chromatography were dried using the standard drying agents according to literature procedures: acetone and ethanol (4Å molecular sieves); diethyl ether, toluene and THF (sodium/benzophenone); dichloromethane ($CaH_2/Na_2SO_4/MgSO_4$); chloroform ($Na_2SO_4/MgSO_4$).[1] Liquid reagents were dried using activated 4Å molecular sieves. Solid reagents were used as supplied unless noted otherwise. Analytical thin layer chromatography was carried out on Merck Kieselgel 60F plates, and visualisation was accomplished by UV light or potassium permanganate. Flash chromatography was performed using Merck Silica Gel 60 (0.040 - 0.063 mm). Kugelrohr distillations were carried out in a Büchi GKR-51 apparatus and the boiling points given correspond to the Kugelrohr oven temperature.

6.0.2 Crystallography

All crystallography data collection and structure refinement was performed by Dr. M.F. Mahon at the University of Bath. The crystallographic data for $[Cu(Hdpa)(NO_3)_2]$, $[Cu(Prdpa)_2(NO_3)_2]$ and $[Cu(Pr_3tacn)(NO_3)_2]$ were recorded on a Nonius KappaCCD diffractometer, while the data for $[Cu(Prdpa)(NO_3)_2]$ were collected using a CAD4 automatic 4-circle diffractometer. Full matrix anisotropic refinement was implemented in the final least-squares cycles throughout. All data were corrected for Lorentz and polarisation, and with the exception of $[Cu(Hdpa)(NO_3)_2]$, for extinction. A multiscan semi-empirical absorption correction was applied to data for $[Cu(Hdpa)(NO_3)_2]$ (maximum and minimum transmission factors were 1.036 and 0.952 respectively). Hydrogen atoms were included at calculated positions throughout. Thermal ellipsoids in illustrations are shown at 30% probability level.

6.0.3 Starting Materials

Starting materials were purchased from Aldrich and the catalyst platinum(0) divinyltetra-siloxane was purchased from Gelest, all were used without further purification. The compounds bis(2-pyridylmethyl)amine, **3**,[2,3] 2-methylamino(*N*-methyl,*N*-2-hydroxyethyl)-pyridine, **5**,[4] 1,4,7-tris(*p*-tosyl)diethylenetriamine, **24**,[5] diethylene glycol ditosylate, **25**,[6] 1-(2-ethoxy)hydroxyethyl-3,8-dioxo-4,7-dimethyl-1,4,7-triazacyclononane, **32**[7] and (2,2-dipyridylamine)copper(II) nitrate, **33**[8] were prepared by literature methods or modifications thereof noted below. The compound *N,N'N''*-tris(*p*-tosyl)-1,4,7-triazacyclononane was prepared by a literature procedure, **34**,[9] and also by the modified method detailed below. Both the ^1H and ^{13}C NMR spectra, as well as IR and microanalyses data were collected for each of these compounds for the sake of completeness, and in order to establish the purity of the products.

All procedures detailed below were performed only after the potential hazards involved in handling and using chemicals had been assessed and the necessary COSHH forms had been completed. Laboratory coats, safety spectacles and protective gloves were worn for all chemical manipulations. Care was taken in the addition of concentrated acidic solutions to concentrated alkali solutions. The $[ClO_4]^-$ anion is strongly oxidising and can be

extremely dangerous to use, especially in organic solvents. Great care was taken when handling any compound containing this anion but it was found to be better than the $[BF_4]^-$ ion in affording pure products.

6.1 General Procedures

6.1.1 Organofunctionalisation of Trisiloxanes via Hydrosilylation

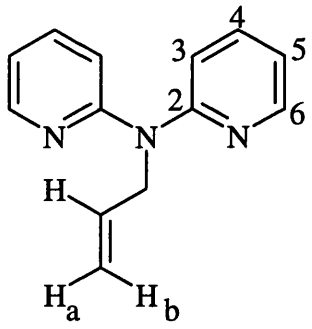
A solution of the terminal alkene-functionalised organic residue (*ca.* 2.0 mmol) in dry toluene (75 ml) was treated in a dry N_2 atmosphere with 1,1,1,3,5,5,5-heptamethyltrisiloxane (*ca.* 2.5 mmol). The reaction mixture was heated under an inert atmosphere to 89 ± 2°C before the catalyst platinum(tetramethyldivinyltetrasiloxane) was added as a 3% solution in xylene (10 μl). Heating was continued for 48 h with additional catalyst being added every 12 h. After removal of solid Pt residues by filtration through a Celite plug, and all volatile materials under reduced pressure, the residue was then purified by Kugelrohr distillation, chromatography, or in one case used as synthesised as only the pure compound remained. Stoichiometries and experimental procedures are detailed in **Section 6.2.1** below for each organofunctionalised trisiloxane prepared.

6.1.2 Membranes Containing Dispersed Solids

Poly(methylhydrosiloxane), $Me_3SiO(MeSi(H)O)_nSiMe_3$ ($n \approx 35$) (0.60 g, 2.64 mmol), a α,ω-poly(disilanol) (6.0 g, 0.33/1.33 mmol) of molecular weight *ca.* 18,000 or *ca.* 4,500 Daltons, tetraethoxysilane (0.60 g, 19.0 mmol), and a weighed quantity of the finely ground solid species were mixed thoroughly in a shallow vessel, either by hand or by sonication (1 s pulses of 20 kHz, for the times indicated in Table 6.1). Care was taken to ensure that the solid was as homogeneously dispersed as possible. Dibutyltindilaurate (0.20-0.43 g, 0.32–0.68 mmol) was then added dropwise with vigorous stirring, until a noticeable increase in the viscosity of the fluid was observed. The viscous mixture was immediately pressed at ambient temperatures between two cellophane sheets to a force of 20 tons for 30 min. The membrane film so produced was cured for several days at 90-100°C until no Si-H absorptions were visible by IR spectroscopy. This procedure also

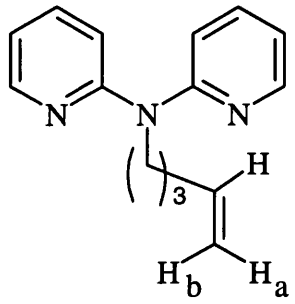
removed unreacted $Si(OEt)_4$ and all volatiles resulting from the cross-linking reaction Membranes produced in this investigation, which are typically 100 ± 20 microns thick, are detailed in **Section 6.3**.

6.2 Acyclic *N*-Donor Ligands



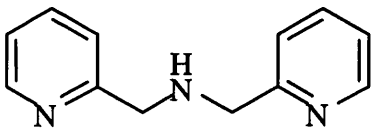
2,2'-Dipyridyl-(*N*-propenyl)amine, Prdpa (1). A solution of 2,2'-dipyridylamine (7.67 g, 44.9 mmol) in THF (150 ml) held at 0°C, was treated with KO^{t}Bu (5.03 g 44.9 mmol) portionwise. The resulting suspension was stirred for 1 h, after which time allyl bromide (3.89 ml, 44.9 mmol) was added dropwise. After stirring for 1 h the precipitated KBr was filtered off, and THF removed from the filtrate under reduced pressure to leave a dark yellow oil. After purification by flash chromatography (silica gel), using hexane-ethyl acetate (1:1) as the eluent, 2.25 g (29 %) of **1** was isolated.

Data: Yellow oil. Analysis: Found (calculated for $C_{13}H_{13}N_3$): C, 73.3 (73.9); H, 6.31 (6.20); N, 19.6 (19.9)%; ^{1}H NMR (270 MHz, $CDCl_3$) 4.86 (2H, d, J = 4.69 Hz, N-C$\underline{H}_2$), 5.40 (1H, dd, C$\underline{H}$aH_b=CH), 5.42 (1H, dd, CHa$\underline{H}_b$=CH), 6.02 (1H, ddt, CH_2-C$\underline{H}$), 6.85 (2H, m, H^5), 7.16 (2H, d, J = 8.59 Hz, H^3), 7.52 (2H, m, H^4), 8.33 (2H, m, H^6) ppm; ^{13}C NMR (68 MHz, $CDCl_3$) 50.3 ($\underline{C}H_2$-N), 114.5 (Ar-$\underline{C}$-H), 115.7 ($\underline{C}H_2$=CH-), 117.0 (Ar-$\underline{C}$-H), 134.7 (CH_2=$\underline{C}$H-), 137.2 (Ar-$\underline{C}$-H), 148.2 (Ar-$\underline{C}$-H), 157.1 (Ar-$\underline{C}$) ppm; IR (liquid film) 1151 (s, N-alkyl), 1282 (s, N-aryl), 1639 (w, C=C), 2855 (w, alkyl-H), 3072 (w, aryl-H) cm^{-1}.



2,2'-Dipyridyl(*N*-pentenyl)amine, Pedpa (2). This was prepared in an analogous manner to Prdpa, using 5-bromo-1-pentene instead of allyl bromide. After purification by flash chromatography, using hexane-ethyl acetate (1:1) as the eluent, 1.18g (11%) of **2** was isolated.

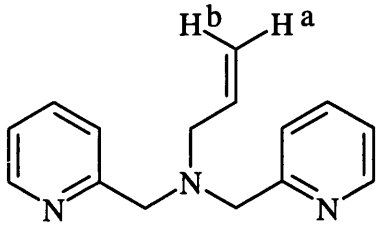
Data: Yellow oil. Analysis: Found (calculated for $C_{15}H_{17}N_3$): C, 74.9 (75.3); H, 7.05 (7.16); N, 17.4 (17.56)%. ^{1}H NMR (270 MHz, $CDCl_3$) 1.81 (2H, m, N-CH_2-C$\underline{H}_2$) 2.12 (2H, q, CH-C$\underline{H}_2$), 4.20 (2H, t, J = 7.51 Hz, N-C$\underline{H}_2$), 4.91 (1H, dd, C$\underline{H}$aH_b=CH), 4.95 (1H, dd, CHa$\underline{H}_b$=CH), 5.83 (1H, ddt, CH_2-C$\underline{H}$), 6.81 (2H, m, H^5), 7.05 (2H, d, J = 8.43 Hz, H^3), 7.47 (2H, m, H^4), 8.31 (2H, m, H^6) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 27.1 ($\underline{C}H_2$-CH_2-N), 31.2 ($\underline{C}H_2$-CH), 47.8 (-$\underline{C}H_2$-N), 114.3 ($\underline{C}H_2$=CH), 114.4 (Ar-$\underline{C}$-H), 116.6 (Ar-$\underline{C}$-H), 136.8 (Ar-$\underline{C}$-H) 138.1 (CH_2=$\underline{C}$H), 148.0 (Ar-$\underline{C}$-H), 157.1 (Ar-$\underline{C}$) ppm; IR (liquid film) 1151 (s, N-alkyl), 1282 (s, N-aryl), 1639 (w, C=C), 2855 (w, alkyl-H), 3072 (w, aryl-H) cm^{-1}.



Bis(2-pyridylmethyl)amine, Hbmpa (3). This tridentate ligand was prepared by two literature methods. Firstly, by the reaction of picolylchloride hydrochloride and 2-methylaminopyridine in the presence of Na_2CO_3 as described by Nelson *et al.* (yield = 29%).[2] It was also prepared by the reductive amination of 2-pyridinecarboxaldehyde and 2-methylaminepyridine in the presence of Na[BH_3CN] as described by McKee *et al.* (yield = 80%).[3]

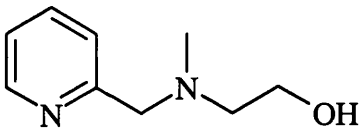
Data: Yellow oil; Analysis: Found (calculated for $C_{12}H_{13}N_3$): C, 69.90 (72.3); H, 6.54 (6.57); N, 20.9 (21.1)%; ^{1}H NMR (270 MHz, $CDCl_3$) 2.88 (1H, s, N$\underline{H}$), 3.98 (4H, s, -$C\underline{H}_2$NHC$\underline{H}_2$-), 7.16 (2H, m, H^5), 7.36 (2H, d, J = 7.8 Hz, H^3), 7.64 (2H, td, J = 4.49, 3.42

Hz, H^4), 8.56 (2H, d, J = 4.88 Hz, H^6) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 54.5 (N-$\underline{C}H_2$-), 121.8 (Ar-$\underline{C}$-H), 122.1 (Ar-$\underline{C}$-H), 136.3 (Ar-$\underline{C}$-H), 149.1 (Ar-$\underline{C}$-H), 159.4 (Ar-$\underline{C}$) ppm; IR (liquid film) 1148 (s, N-alkyl), 1298 (w, N-aryl), 3054 (s, aryl-H), 3309 (m, N-H) cm^{-1}.



Bis-(2-pyridylmethyl)(*N*-propenyl)amine, Prbmpa (4). 3 (0.25 g, 1.25 mmol) dissolved in THF (50 ml), was reacted with KO^{t}Bu (0.14 g, 1.25 mmol), and the reaction mixture stirred for 1 h. Allyl bromide (0.15 g, 1.25 mmol) was then added, and the solution was stirred for 48 h. After this time the insoluble KBr was removed by filtration, and all volatiles removed from the filtrate under reduced pressure. The residue was purified by chromatography (alumina) using 40-60° petroleum ether/ethyl acetate (3:2) as the eluent. The desired product was collected from the first band eluted. Fractions containing this band were combined and the solvent was removed under reduced pressure to leave 0.13 g (43%) of **4**.

Data: Brown oil; Analysis: Found (calculated for $C_{15}H_{17}N_3$): C, 72.9 (75.3); H, 7.27 (7.16); N, 16.5 (17.6)%; ^1H NMR (270 MHz, $CDCl_3$) 3.19 (2H, d, J = 6.48 Hz, N-$\underline{C}H_2$-), 3.82 (4H, s, -$\underline{C}H_2NHC\underline{H}_2$-), 5.20 (1H, dd, $C\underline{H}_aH_b$=CH-), 5.22 (1H, dd, $CH_a\underline{H}_b$=CH-), 5.94 (1H, ddt, -$\underline{C}H$=CH_2), 7.14 (2H, m, H^5), 7.54 (2H, d, J = 7.78 Hz, H^3), 7.65 (2H, m, H^4), 8.53 (2H, m, H^6) ppm; ^{13}C NMR (68 MHz, $CDCl_3$) 57.3 ($\underline{C}H_2$-N-$\underline{C}H_2$), 59. 9 (N-$\underline{C}H_2$-CH), 118.0 ($\underline{C}H_2$=), 121.9 (Ar-$\underline{C}$-H), 122.8 (Ar-$\underline{C}$-H), 135.4 ($\underline{C}$H=), 136.4 (Ar-$\underline{C}$-H), 149.0 (Ar-$\underline{C}$-H), 159.8 (Ar-$\underline{C}$) ppm; IR (liquid film)1149 (s, N-alkyl) 1297(w, N-aryl), 1681 (s, C=C), 3064 (s, aryl-H) cm^{-1}.

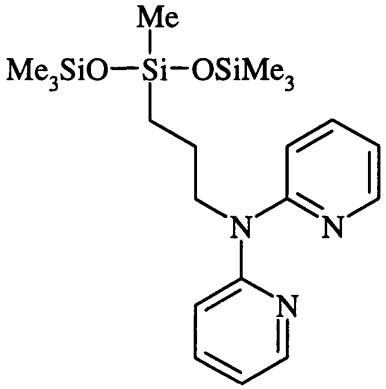


2-Methylamino(*N*-methyl-*N*-2-hydroxylethyl)pyridine, Mamp (5). A solution of 2-chloro-methylpyridine hydrochloride (2.00 g, 12.2 mmol) in H_2O (10 ml) was neutralised with a saturated aqueous solution of K_2CO_3. The solution was held at 0°C before being treated with a solution of *N*-methylethanolamine (0.92 g, 12.2 mmol) and powdered KOH (0.68g, 12.2 mmol) in EtOH (30 ml). The reaction mixture was then heated at 45°C for 5 h, and on cooling the solvent was removed under reduced pressure. The residue was dissolved in 10M NaOH solution (10 ml) and was extracted with CH_2Cl_2 (2 x 50 ml). The organic phases were combined and dried (Na_2SO_4), and the solvent removed under reduced pressure. The residue was distilled (Kugelrohr) and the fraction collected at 175°C, 0.8 mmHg (lit value[4]: 120 @ 0.6 mmHg), yielded 1.16 g (57 %) of **5**.

Data Yellow oil; Analysis: Found (calculated for $C_9H_{14}N_2O$): C, 63.6 (65.0); H, 8.44 (8.49); N, 16.2 (16.6)%; ^{1}H NMR ($CDCl_3$, 270 MHz) 2.34 (2H, s, C$\underline{H}_2$-N) 2.64 (2H, t, J = 5.50 Hz, N-C$\underline{H}_2$-CH_2), 3.68 (2H, t, J = 5.31 Hz, -C$\underline{H}_2$-OH), 3.74 (3H, s, N-C$\underline{H}_3$), 4.05 (1H, s, O$\underline{H}$), 7.18 (1H, m, H^5), 7.41 (1H, d, J = 7.1 Hz, H^3), 7.66 (1H, m, $\underline{H}^4$), 8.55 (1H, m, $\underline{H}^6$) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) 42.4 ($\underline{C}H_3$), 58.9 ($\underline{C}H_2$), 63.1 ($\underline{C}H_2$), 64.3 (CH_2), 121.9 (Ar-$\underline{C}$-H), 122.9 (Ar-$\underline{C}$-H), 136.4 (Ar-$\underline{C}$-H), 148.7 (Ar-$\underline{C}$-H) 158.4 (Ar-$\underline{C}$) ppm; IR (liquid film) 1121 (s, N-alkyl) 1304(w, N-aryl), 3060 (s, aryl-H), 3422 (OH stretch) cm^{-1}.

6.2.1 Organofunctionalised Trisiloxanes

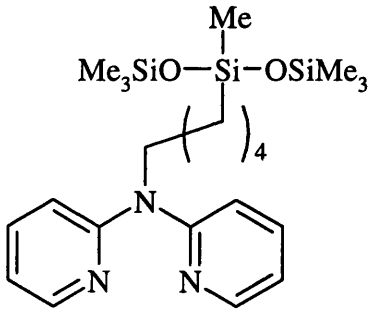
All trisiloxanes in this section were synthesised using the general procedure as detailed in Section **6.1.1**. Methods of purification and analyses for all compounds are presented below.



3-(3-(2,2'dipyridylamino)propyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (6).

After removal of volatile materials, under reduced pressure, the residue was purified by Kugelrohr distillation. The first fraction collected (100°C, 0.3 mmHg) was identified as unreacted Prdpa, the second fraction (150°C, 0.3 mmHg) yielded 0.24 g (29%) of **6**.

Data: Yellow oil; Analysis: Found (calculated for $C_{20}H_{35}N_3O_2Si_3$): C, 55.7 (55.4); N, 9.69 (9.69); H, 8.09 (8.13)%; ^{1}H NMR (400 MHz, $CDCl_3$) 0.02 (21H, m, Si-C$\underline{H}_3$), 0.52 (2H, m, Si-C$\underline{H}_2$), 1.73 (2H, m, CH_2-C$\underline{H}_2$), 4.15 (2H, t, J = 7.61 Hz, C$\underline{H}_2$-N), 6.85 (2H, m, $\underline{H}^2$), 7.12 (2H, m, $\underline{H}^4$), 7.52 (2H, m, $\underline{H}^3$), 8.34 (2H, m, $\underline{H}^1$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 14.9 (Si-$\underline{C}H_2$), 21.8 (CH_2-$\underline{C}H_2$-CH_2), 51.3 ($\underline{C}H_2$-N), 114.6 (Ar-$\underline{C}$-H), 116.6 (Ar-$\underline{C}$-H), 136.8 (Ar-$\underline{C}$-H), 148.1 (Ar-$\underline{C}$-H), 157.3 (Ar-C) ppm; ^{29}Si (79 MHz, $CDCl_3$) –21.7 (CH_3-$\underline{Si}(O)_2$-CH_2), 7.0 ($\underline{Si}(CH_3)_3$) ppm.

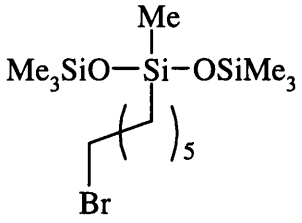


3-(3-(2,2'dipyridylamino)pentenyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (7).

After removal of volatile materials, under reduced pressure, the residue was purified by removal of unreacted Pedpa by Kugelrohr distillation. Yield 0.1 g (52%) of **7**

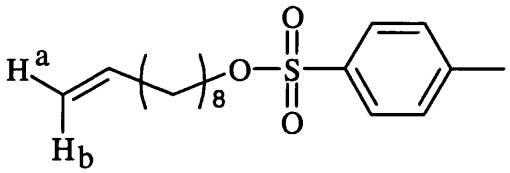
Data: Yellow oil; Analysis: Found (calculated for $C_{22}H_{39}N_3O_2Si_3$): C, 56.2 (57.2); N, 9.33 (9.10); H, 8.10 (8.51)%; ^{1}H NMR (400 MHz, $CDCl_3$) 0.02 (21H, m, Si-C$\underline{H}_3$), 0.46 (2H, m, Si-C$\underline{H}_2$), 1.36 (4H, m, -C$\underline{H}_2$-C$\underline{H}_2$-), 1.71 (2H, m, C$\underline{H}_2$-CH_2-N), 4.15 (2H, t, J = 7.61 Hz,

$C\underline{H}_2$-N), 6.85 (2H, m, $\underline{H}^2$), 7.12 (2H, m, $\underline{H}^4$), 7.52 (2H, m, $\underline{H}^3$), 8.34 (2H, m, $\underline{H}^1$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) -0.13 (Si-$\underline{C}H_3$), 2.01 (Si($\underline{C}H_3)_3$), 17.8 (Si-$\underline{C}H_2$), 23.1 (Si-CH_2-$\underline{C}H_2$), 28.1 (Si-CH_2-CH_2-$\underline{C}H_2$), 30.7 ($\underline{C}H_2$-CH_2-N), 48.4 ($\underline{C}H_2$-N), 114.6 (Ar-$\underline{C}$-H), 116.7 (Ar-$\underline{C}$-H), 136.9 (Ar-$\underline{C}$-H), 148.2 (Ar-$\underline{C}$-H), 157.4 (Ar-C) ppm; ^{29}Si (79 MHz, $CDCl_3$) -21.4 (CH_3-$\underline{Si}(O)_2$-CH_2), 6.79. ($\underline{Si}(CH_3)_3$) ppm.



1,1,1,3,5,5,5-Heptamethyl-3-(6-bromohexyl)-trisiloxane (8). After filtration the solvent and volatile materials were removed under reduced to pressure to yield 1.25 g (83%) of pure **8**.

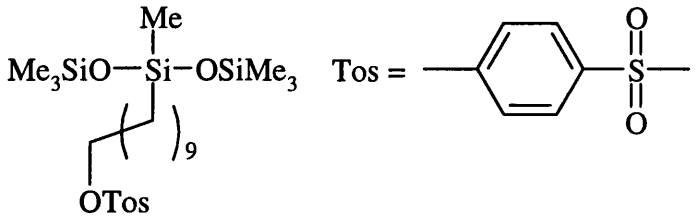
Data: Yellow oil; Analysis: Found (calculated for $C_{13}H_{33}O_2Si_3Br$): C, 40.6 (40.5); H, 8.57 (8.56)%; ^{1}H NMR (270 MHz, $CDCl_3$) 0.14 (21H, m, $C\underline{H}_3$-Si-), 0.53 (2H, t, J = 3.39 Hz, Si-$C\underline{H}_2$-CH_2-), 1.41 (6H, m, Si-CH_2-$C\underline{H}_2$-$C\underline{H}_2$-$C\underline{H}_2$-), 1.91 (2H, p, J = 7.14 Hz, -$C\underline{H}_2CH_2Br$), 3.48 (2H, t, J = 6.87 Hz, $C\underline{H}_2$-Br) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) -0.28 ($\underline{C}H_3$-Si-CH_2), 1.85 ($\underline{C}H_3$-Si-O-), 17.5 (Si-$\underline{C}H_2$-), 22.9 (Si-CH_2-$\underline{C}H_2$-), 27.9 (-CH_2-$\underline{C}H_2$), 32.3 (-$\underline{C}H_2$-CH_2-), 32.8 (-$\underline{C}H_2$-CH_2Br), 34.0 ($\underline{C}H_2$-Br) ppm.



Dec-9-enyl-4-methylbenzenesulphonate (9). To a solution of 9-decen-1-ol (2.00 g, 12.8 mmol) in diethyl ether (50 ml) was added powdered KOH (0.72 g, 12.8 mmol) portionwise. The suspension was cooled to 0°C before *p*-toluenesulfonylchloride (2.36 g, 12.5 mmol) was also added portionwise. The mixture was then allowed to warm slowly to room temperature and was stirred for a further 72 h. After removal of any insoluble material by filtration the filtrate was extracted with water (2 x 20 ml) followed by saturated brine solution (1 x 20 ml). The aqueous extracts were discarded and the ether layer was

dried (Na_2SO_4) before the solvent was removed under reduced pressure. The residue was purified by chromatography (silica gel) using CH_2Cl_2 as the eluent to yield 3.74 g (64%) of **9**.

Data: White solid; Analysis: ^1H NMR (270 MHz, $CDCl_3$) 1.23 (10H, m, -($C\underline{H}_2$)CH_2CH_2OTs), 1.63 (2H, qu, J = 6.78 Hz, $C\underline{H}_2CH_2OTs$), 2.02 (2H, m, CH_2=$CHC\underline{H}_2$), 2.45 (3H, s, Ar-$C\underline{H}_3$), 4.01 (2H, t, J = 6.41 Hz, $CH_2C\underline{H}_2OTs$), 4.99 (1H, dd, $C\underline{H}_aH_b$=CH-), 4.92 (1H, dd, $CH_a\underline{H}_b$=CH-), 5.75 (1H, ddt, CH_2=$C\underline{H}$), 7.35 (2H, d, J = 7.88 Hz, Ar-$\underline{H}$), 7.79 (2H, d, J = 8.42 Hz, Ar-H) ppm; ^{13}C NMR (67.8 MHz, $CDCl_3$) 21.63 (Ar-$\underline{C}H_3$), 25.30, 28.80, 28.84, 28.93, 29.21 (-($\underline{C}H_2$)$_6CH_2CH_2$-O-Ar), 33.75 ($\underline{C}H_2CH_2$-O-Ar), 70.69 ($\underline{C}H_2$-O-Ar), 114.20 $\underline{C}H_2$=CH), 127.88 (Ar-$\underline{C}$-H), 129.81 (Ar-$\underline{C}$-H), 133.24 (Ar-$\underline{C}$), 139.08 (CH_2=$\underline{C}$H), 144.65 (Ar-$\underline{C}$) ppm.



1,1,1,3,5,5,5-heptamethyl-3-(10-(tosyl)decyl)trisiloxane (10).

Purified by chromatography on silica gel using hexane/ethyl acetate (30:1) as the eluent. Yield 1.40 g (92%) of **10**.

Data: Colourless liquid; Analysis: ^1H NMR (270 MHz, $CDCl_3$) 0.02 (21H, m, $SiCH_3$), 0.37 (2H, m, $SiCH_2$), 1.15 (14H, m, $SiCH_2(C\underline{H}_2)_7CH_2CH_2$-O-Ar), 1.54 (2H, m, $C\underline{H}_2CH_2$-O-Ar), 2.38 (3H, s, Ar-$C\underline{H}_3$), 3.95 (2H, t, J = 6.41 Hz, $CH_2C\underline{H}_2$-O-Ar), 7.27 (2H, d, J = 8.06 Hz, Ar-H), 7.72 (2H, d, J = 8.42 Hz, Ar-H) ppm; ^{13}C NMR (67.8 MHz, $CDCl_3$) -0.29, 1.85 (Si-$\underline{C}H_3$), 17.60 (Si-CH_2), 23.04, 25.31, 28.79, 28.92, 29.89, 29.40 (Si-$CH_2(\underline{C}H_2)_7$), 33.18 ($\underline{C}H_2CH_2$-O-Ar), 70.69 ($\underline{C}H_2$-O-Ar), 127.86 (Ar-$\underline{C}$-H), 129.76 (Ar-$\underline{C}$-H), 132.66 (Ar-C), 144.56 (Ar-C) ppm.

6.3 Membranes Containing Dispersed Solids

Siloxane membranes containing dispersed solids were all prepared as described in **Section 6.1.2** above. Those with low solid loadings were strong, highly flexible films, whereas high loadings of inorganic solids decreased the tensile strength of the film.

No.	Dispersed Species	% Loading (w/w).	Method of dispersion.	Length of time in sonicator (mins).
11	Charcoal (Activated with 12% w/w $KMnO_4$)	12	Hand Mixing	N/A
12	Charcoal	25	Hand Mixing	N/A
13	Charcoal	25	Sonication	12
14	Charcoal	30	Sonication	12
15	Charcoal	30	Sonication	30
16	Silica	15	Hand Mixing	N/A
17	$Cu(OH)_2$	5	Hand Mixing	N/A
18	$Cu(OH)_2$	12	Hand Mixing	N/A
19	$Cu(OH)_2$	20	Hand Mixing	N/A
20	$Cu(OH)_2$	25	Sonication	30
21	$Zn(OH)_2$	5	Hand Mixing	N/A
22	$Zn(OH)_2$	12	Hand Mixing	N/A
23	$Zn(OH)_2$	20	Hand Mixing	N/A

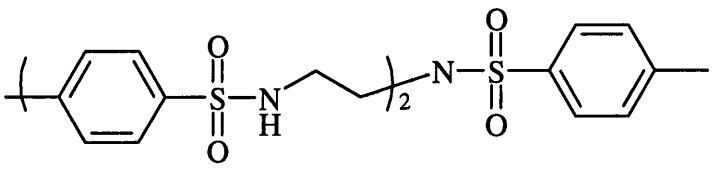
Table 6.1. Preparation of membranes containing dispersed species.

6.4 Cyclic *N*-Donor Ligands

6.4.1 1,4,7-Triazacyclononane, H_3tacn

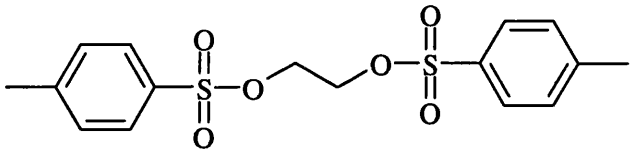
The title compound was synthesised using the route as described by Hay[9] in which a sulfonamide protected, linear triamine is reacted with a bis-sulfonate ester to produce the corresponding cyclic tri-sulfonamide. This compound is then deprotected to yield the cyclic triamine, which is isolated as the trihydrochloride salt. The linear triamine, 1,4,7-tris(*p*-tosyl)diethylenetriamine[5], and the bis-sulfonate ester diethylene glycol ditosylate[6] were prepared by literature procedures. The ring closure reaction was performed successfully using either the literature methodology as described by Hay[9], or the modified procedure as detailed below. The deprotection reaction was attempted numerous times

using literature procedures but all failed[9,10] and so a modified procedure, also detailed below, was finally used.



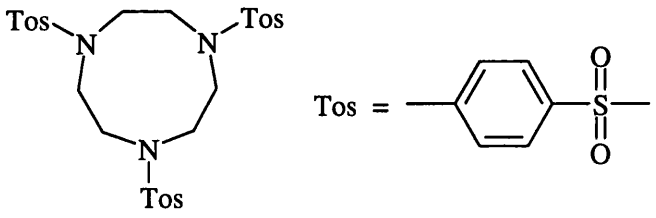
1,4,7-Tris(*p*-tosyl)diethylenetriamine (24).

Data: Yellow solid; Analysis: Found (calculated for $C_{25}H_{31}N_3O_6S_2$); C, 52.70 (53.10); H, 5.44 (5.49); N, 7.40 (7.43)%; ^{1}H NMR (270 MHz, $CDCl_3$) 1.25 (2H, s, NH), 2.43 (9H, s, CH_3), 3.16 (8H, q, J = 4.58 Hz, CH_2-CH_2), 7.31 (6H, d, J = 7.88 Hz, Ar-H), 7.61 (2H, d, J = 8.43 Hz, Ar-H), 7.61 (4H, d, J = 8.24 Hz, Ar-H) ppm; ^{13}C NMR (100.40 MHz, $CDCl_3$) 21.5 (CH_3), 42.7 (CH_2), 50.5 (CH_2), 127.3 (Ar-C-H), 127.4 (Ar-C-H), 129.9 (Ar-C-H), 130.1 (Ar-C-H), 135.2 (Ar-C), 137.1 (Ar-C), 143.7 (Ar-C), 144.2 (Ar-C) ppm.



Diethylene glycol ditosylate (25).

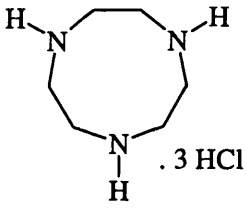
Data: White solid; Analysis: Found (calculated for $C_{16}H_{18}O_6S_2$); C, 51.5 (51.9); H, 5.0 (4.90)%; ^{1}H NMR (270 MHz, $CDCl_3$) 2.46 (6H, s, CH_3), 4.18(4H, s, CH_2-CH_2), 7.34 (4H, d, J = 8.06 Hz, Ar-H), 7.74 (4H, d, J = 8.43 Hz, Ar-H) ppm; ^{13}C NMR (67.8 MHz, $CDCl_3$) 21.7 (CH_3), 66.7 (CH_2-CH_2), 128.0 (Ar-C-H), 130.0 (Ar-C-H), 132.4 (Ar-C), 145.3 (Ar-C) ppm.



***1,4,7*-Tris(*p*-tosyl)-1,4,7-triazacyclononane (26).** The procedure outlined below is based on a modification of that reported by Hay[9] A solution of **24** (3.27 g, 5.34 mmol) in dry

DMF (50 ml) was treated with an excess of NaH (60% mineral oil dispersion) (0.384 g, 16.0 mmol) under a N_2 atmosphere. The resulting mixture was stirred for an hour or until hydrogen evolution had ceased. The solution was then filtered under an inert atmosphere and the filtrate heated to 90°C. To this was added a solution of **25** (2.41 g, 6.51 mmol) in dry DMF (20 ml) over 45 min. The temperature was raised to 105°C and heating was continued for a further 4 h. The solution was then cooled to room temperature and poured slowly and carefully into water (100 ml). The resulting precipitate was collected and recrystallised from EtOH/H_2O to yield 5.65 g (56 %) of **26**.

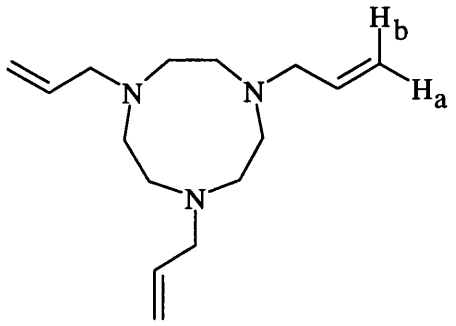
Data: White solid; Analysis: Found (calculated for $C_{27}H_{33}N_3O_6S_3$): C, 54.6 (54.8); H, 5.6 (5.62); N, 7.1 (7.10)%; ^{1}H NMR (270 MHz, $CDCl_3$) 2.44 (9H, s, C<u>H</u>$_3$), 3.42 (12H, s, C<u>H</u>$_2$-C<u>H</u>$_2$), 7.33 (6H, d, J = 8.06 Hz, Ar-<u>H</u>), 7.70 (6H, d, J = 8.25 Hz, Ar-<u>H</u>) ppm; ^{13}C NMR (67.80 MHz, $CDCl_3$) 21.5 (<u>C</u>H$_3$), 51.9 (<u>C</u>H$_2$-<u>C</u>H$_2$), 127.5 (Ar-<u>C</u>-H), 129.9 (Ar-<u>C</u>-H) 134.9 (Ar-<u>C</u>), 143.9 (Ar-<u>C</u>) ppm.



1,4,7-Triazacyclononane trihydrochloride (27). A solution of **26** (4.12 g, 6.96 mmol) in 98% H_2SO_4 (25 ml) was heated to 120°C for 48 h. On cooling to room temperature the acidic solution was slowly added (CAUTION) to a solution of 10M NaOH (150 ml) held at 0°C in an ice bath. The pH of the resulting solution was adjusted to pH 14 or greater, and left overnight to allow precipitation of Na_2SO_4, which was subsequently removed by filtration. The filtrate was then extracted with $CHCl_3$ (5 x 250 ml), and the organic extracts were combined. The solvent was removed under reduced pressure and the resulting residue was dissolved in EtOH (30 ml). Any insoluble material was removed by filtration, and precipitation of a white solid occurred on addition of concentrated HCl (10 ml) to the filtrate. The solid was collected and recrystallised from 2M HCl and ethanol before being dried at 65°C in a vacuum oven to yield 0.91 g (55%) of **27**.

Data: White hygroscopic solid; Analysis: Found (calculated for $C_6H_{18}N_3Cl_3$) C, 29.6 (30.2); H, 7.50 (7.60); N, 17.2 (17.6)%; ^{1}H NMR (400 MHz, D_2O) 3.35 (12H, s, C<u>H</u>$_2$) ppm; ^{13}C NMR (67.9 MHz, $CDCl_3$) 45.0 (N-<u>C</u>H$_2$-<u>C</u>H$_2$-N) ppm.

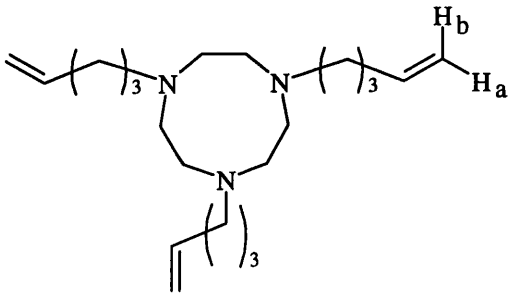
6.4.2 Symmetrically Substituted H_3tacn Derivatives



1,4,7-Tri-(*N*-propenyl)-1,4,7-triazacyclononane (28). Method 1: To a solution of **27** (0.50 g, 2.10 mmol) in MeCN/Et_2O, (1:1, 50 ml), under an inert atmosphere, was added NEt_3 (g, 6.30 mmol) and the suspension was stirred overnight so producing a pale yellow solution containing a little solid. After the insoluble material was removed by filtration under an inert atmosphere, the solvent and any unreacted NEt_3 were removed from the filtrate under reduced pressure. The residue was then dissolved in toluene/EtOH (2:1, 50 ml) before the addition of allyl bromide (0.89 g, 7.36 mmol) and powdered KOH (3.00 g, 53.5 mmol). The solution was then stirred for 24 h after which time the solvent was removed under reduced pressure and the residue washed several times with Et_2O. The ether washings were combined and the solvent removed to leave 0.29 g (57%) of **28**.

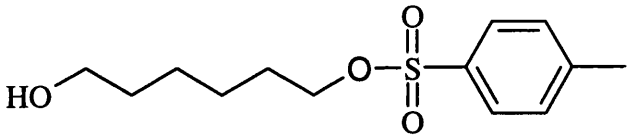
Method 2: This is a modification of a synthetic methodology described by Peacock *et al.* for the synthesis of 1,4,7-tri-(*N*-propynyl)-1,4,7-triazacyclononane[11].To a suspension of **27** (0.50 g, 2.10 mmol) in Et_2O, (50 ml) was added KOH pellets (3.00 g, 53.5 mmol). The suspension was stirred overnight, under an inert atmosphere, so producing a pale yellow solution. This was treated with allyl bromide (0.89 g, 7.36 mmol) and stirring was continued for a further 24 h. Insoluble material was removed by filtration under an inert atmosphere and the volatiles were removed under reduced pressure to leave 0.42 g (80%) of **28**.

Data: Yellow oil; Analysis: Found (calculated for $C_{15}H_{27}N_3$): C, 71.3 (72.2); H, 10.8 (10.9); N, 15.6 (16.9)%; ^{1}H NMR (270 MHz, $CDCl_3$) 2.75 (12 H, s, N-C$\underline{H}_2$-C$\underline{H}_2$-N), 3.14 (6 H, d, J = 6.41, C$\underline{H}_2$-CH), 5.01 (1H, dd, C$\underline{H}_a$H$_b$=CH-), 5.05 (1H, dd, CH$_a$$\underline{H}_b$=CH-), 5.89 (3H, ddt, =C$\underline{H}$-) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 55.3 (N-$\underline{C}H_2$-$\underline{C}H_2$-N), 61.9 ($\underline{C}H_2$-CH), 116.4 ($\underline{C}H_2$=CH), 136.8 ($\underline{C}$H=CH$_2$) ppm; IR (liquid film) 1154 (s, N-alkyl), 1640 (w, C=C), 2787 (w, alkyl-H), 3072 (w, alkenyl-H) cm^{-1}.



1,4,7-Tri(*N*-pentenyl)triazacyclononane (29). This was prepared using a modification of the procedure for the synthesis of 1,4,7-tri(*N*-isopropyl)triazacyclononane[12] A suspension of **27** (1.00 g, 4.2 mmol) in MeCN (20 ml) was treated with excess NEt_3 (1.27 g, 12.6 mmol). The resulting suspension was then stirred for an hour to ensure that all of the free amine had reacted. The solution was then filtered to remove the resultant NEt_3·HCl, and the filtrate was diluted with toluene (50 ml). 5-Bromo-1-pentene (1.87 g, 12.6 mmol) was then added, and the solution heated to 80-90°C for 3 h. After addition of KOH (5.00 g, 89.1 mmol) the hot mixture was stirred for a further 5 h. After filtration the solvent was removed from the filtrate under reduced pressure and the resulting residue was dissolved in MeOH (50 ml). Solid $NaClO_4$ (3 g, 24.5 mmol) was added to the MeOH solution with vigorous stirring, followed by sufficient H_2O to produce turbidity. Refrigeration at 0°C for 2 h resulted in precipitation of the mono-hydroperchlorate salt, [HPe_3tacn][ClO_4], which was collected, dissolved in toluene (50 ml) (CAUTION) and stirred over KOH (7.00 g, 124.8 mmol) for 18 h. Filtration followed by removal of the solvent from the filtrate under reduced pressure yielded, 0.65 g (47%) of **29**.

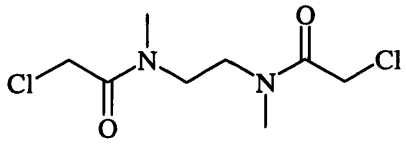
Data: Yellow oil; Analysis: Found (calculated for $C_{21}H_{39}N_3$): C, 76.1 (75.6); H, 11.7 (11.8); N, 12.6 (12.6)%; ^{1}H NMR (270 MHz, $CDCl_3$) 1.54 (6H, p, J = 7.3 Hz, CH_2-C$\underline{H}_2$-CH_2), 2.07 (6H, q, J = 6.6 Hz, C$\underline{H}_2$-CH=), 2.47 (6H, t, J = 7.33 Hz, N-C$\underline{H}_2$) 2.72 (12 H, s, N-C$\underline{H}_2$-C$\underline{H}_2$-N), 4.96 (1H, dd, C$\underline{H}_a$H$_b$=CH-), 4.99 (1H, dd, CH$_a$H$_b$=CH-), 5.82 (3H, ddt, =C$\underline{H}$-) ppm; ^{13}C NMR (67.9 MHz, $CDCl_3$) 27.3 (CH_2-$\underline{C}H_2$-CH_2), 31.7 (N-$\underline{C}H_2$-, 55.9 (N-$\underline{C}H_2$-$\underline{C}H_2$-N), 58.4 ($\underline{C}H_2$-CH), 114.3 ($\underline{C}H_2$=CH), 138.8 ($\underline{C}$H=CH_2) ppm; IR (liquid film) 1100 (s, alkyl-N)1640 (w, C=C), 2858(s, alkyl-H) 3076 (s, alkenyl-H) cm^{-1}.



1-Tosyl-6-hexanol (30). To a solution of hexanediol (2.00 g, 16.9 mmol) in Et_2O (50 ml) was added powdered potassium hydroxide (0.61 g, 9.30 mmol). To this suspension was added 4-methylbenzylsulphonyl chloride (1.61 g, 8.46 mmol), with caution. Stirring was continued under a nitrogen atmosphere for 21 h. The reaction mixture was filtered and the filtrate was washed with water (2 × 20 ml) and brine (20 ml) and dried (Na_2SO_4). The solvent was removed by evaporation to give 1.60 g (69%) of **30** after chromatography on silica gel using CH_2Cl_2/MeOH (20:1) as the eluent.

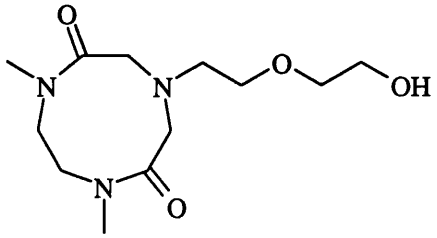
Data: Colourless oil; ^{1}H NMR (270 MHz, $CDCl_3$) 1.33 (4H, m, -($C\underline{H}_2$)$_2C\underline{H}_2C\underline{H}_2$-O-Ar), 1.52 (2H, qu, J = 6.60 Hz, HO-$CH_2C\underline{H}_2$), 1.66 (2H, qu, J = 7.33 Hz, -$C\underline{H}_2CH_2$-O-Ar), 2.45 (3H, s, Ar-$C\underline{H}_3$), 3.60 (2H, t, J = 6.60 Hz, $C\underline{H}_2$-OH), 4.02 (2H, t, J = 6.42 Hz, $C\underline{H}_2$-O-Ar), 7.35 (2H, d, J = 7.88 Hz, Ar-C-H), 7.79 (2H, d, J = 8.43 Hz, Ar-C-H) ppm.

6.4.3 Asymmetrically Substituted H_3tacn Derivatives



***N,N'*-Bis-methyl-*N,N'*-bis-chloracetyl-ethylendiamine (31).** Chloroacetylchloride (7.69 g, 68.1 mmol) was dissolved in dry, degassed $CHCl_3$ and the solution was heated to reflux. To this was added *N,N'*-dimethylethylenediamine (3.00 g, 34.0 mmol) over a 5 h period, and heating was continued for a further 1 h. Once cool the reaction mixture was filtered and volatiles were removed under reduced pressure. The resulting solid residue was recrystallised from EtOH/Et_2O to yield 5.10 g (62%) of **31**

Data: White solid; Analysis: Found (calculated for $C_8H_{14}N_2O_2Cl_2$): C, 39.1 (39.9); H, 6.05 (5.85); N, 11.9 (11.6)%; ^{1}H NMR (270 MHz, $CDCl_3$) 3.13 (6H, s, $C\underline{H}_3$-N), 3.61 (4H, s, $C\underline{H}_2$-N), 4.05 (4H, s, $C\underline{H}_2$-Cl) ppm; ^{13}C NMR (67.94 MHz, $CDCl_3$) 36.0 ($\underline{C}H_3$-N), 41.4 ($\underline{C}H_2$-N), 45.2 ($\underline{C}H_2$-Cl), 167.2 ($\underline{C}$=O) ppm.



1-(2-ethoxy)hydroxyethyl-3,8-dioxo-4,7-dimethyl-1,4,7-triazacyclononane (32).

Solid **31** (2.78 g, 11.5 mmol) was dissolved in MeCN (100 ml), and treated with 2-(2-aminoethoxy)ethanol (061 g, 5.75 mmol), LiBr (0.02 g, 0.23 mmol) and Na_2CO_3 (3.67 g, 34.6 mmol). The resulting suspension was heated under reflux for 24 h. The reaction mixture was cooled, filtered, and the volatiles removed from the filtrate under reduced pressure. The resulting residue was purified by chromatography (silica gel), using CH_2Cl_2:MeOH (2:1) as the eluent, to leave 1.07 g (34%) of **32**.

Data: Yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) 2.95 (2H, t, J = 5.13 Hz, N-C$\underline{H}_2$-CH$_2$-O), 3.01 (6H, s, C$\underline{H}_3$-N), 3.51 (4H, s, N-C$\underline{H}_2$-C$\underline{H}_2$-N), 3.59 (2H, t, J = 4.76 Hz, O-CH$_2$-C$\underline{H}_2$-OH), 3.66 (2H, t, J = 4.95 Hz, N-CH$_2$-C$\underline{H}_2$-O), 3.74 (2H, t, J = 4.58 Hz, O-CH$_2$-C$\underline{H}_2$-OH), 3.81 (4H, s, C-C$\underline{H}_2$-N) ppm; ^{13}C NMR (67.94 MHz, $CDCl_3$) 37.5 (C$\underline{H}_3$-N), 51.0 (N-C$\underline{H}_2$-C$\underline{H}_2$-N), 55.7 (N-C$\underline{H}_2$-CH$_2$-O), 58.5 (C-C$\underline{H}_2$-N), 61.6 (N-CH$_2$-C$\underline{H}_2$-O), 68.6 (O-C$\underline{H}_2$-CH$_2$-OH), 72.4 (C$\underline{H}_2$-OH), 170.5 (C=O) ppm; IR (liquid film) 1121 (s, N-alkyl), 1634 (s, C=O stretch), 3397 (br, OH stretch) cm^{-1}.

6.5 Metal Complexes of *N*-Donor Ligands

6.5.1 Complexes of Acyclic N-Donor Ligands

6.5.1.1 Cu(II) Adducts of Rdpa (R = H or Propenyl)

[Cu(Hdpa)$_2$(NO$_3$)$_2$] (33). This complex was prepared by a modification of the method described by McWhinnie[8]. To a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.24 g, 0.99 mmol) in MeOH (8 ml) was added Hdpa (0.34g, 1.98 mmol) also dissolved in MeOH (8 ml). The reaction vessel was sealed and the solution was stirred for an hour, after which time a green precipitate had formed. The product was collected and recrystallised from water to give 0.20 g (38%) of **33**.

Data: Olive green crystals; Analysis: Found (calculated for $C_{20}H_{18}N_8O_6Cu$): C, 43.8 (45.3); N, 20.5 (21.1); H, 3.29 (3.42)%; IR (nujol mull) 1019 (w, ν_{sym} NO_2), 1269 (s, ν_{asym} NO_2), 1288 (s, N-aryl), 1468 (s, ν_{asym} NO_2) cm^{-1}.

[Cu(Prdpa)$_2$(NO$_3$)$_2$] (34). To a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.28 g, 1.2 mmol) in EtOH (8 ml) was added **1** (0.50 g, 2.4 mmol) also in EtOH (8 ml). The reaction vessel was sealed and the solution was stirred for an hour at 0°C. The precipitate which had formed was collected and recrystallised from MeOH to yield 0.48 g (66%) of **34**.
Data: Purple crystals; Analysis: Found (calculated for $C_{26}H_{26}N_8O_6Cu$): C, 50.8 (51.2); N, 17.5 (18.4); H, 4.25 (4.30)%; IR (nujol mull) 1026 (w, ν_{sym} NO_2), 1163 (s, N-alkyl), 1268 (s, ν_{asym} NO_2), 1288 (s, N-aryl), 1471 (s, ν_{asym} NO_2) 1601 (s, C=C stretch) cm^{-1}.

[Cu(Prdpa)(NO$_3$)$_2$] (35). Method 1. A solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.57 g, 2.4 mmol) in EtOH (8 ml) was treated with a solution of **1** (0.50 g, 2.4 mmol) in EtOH (8 ml). The reaction vessel was sealed and the solution was stirred for an hour. The resultant purple precipitate was collected and the filtrate was concentrated by rotary evaporation. A green product was precipitated from the filtrate on treatment with Et_2O. After collection the solid was dissolved in CH_2Cl_2 (5 ml) and cyclohexane was added dropwise until turbidity just persisted. Refrigerating the sample overnight completed precipitation, collection of the solid yielded 0.10 g (12%) of **35**.
Method 2. To a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.14 g, 4.1 mmol) in acetone (10 ml) was added a solution of **1** (0.12 g, 4.1 mmol) in acetone (8 ml). The solution was stirred for an hour and the resulting green solid collected by filtration. It was purified in the same manner as before to yield 0.04 g (18%) of **35**.
Data: Dark green crystals. Analysis: Found (calculated for $C_{13}H_{13}N_5O_6Cu$): C, 37.70 (39.15); N, 16.40 (17.56); H, 3.06 (3.28); IR (nujol mull) 1008 (s, ν_{sym} NO_2), 1161 (s, N-alkyl) 1271 (s, ν_{asym} NO_2), 1288 (s, N-aryl), 1491 (w, ν_{asym} NO_2) 1604 (s, C=C stretch) cm^{-1}.

[Cu(Hdpa)(NO$_3$)$_2$] (36). To a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (1.0 g, 4.1 mmol) in MeOH (10 ml) was added a solution of Hdpa (0.71 g, 4.1 mmol) in MeOH (8 ml). The solution was stirred for an hour after which time a green solid had precipitated. Et_2O was added to

complete precipitation of the solid, which was collected by filtration, washed with Et_2O, dried and recrystallised from MeOH to afford 1.39 g (93%) of **36**.

Data: Light green crystals. Analysis: Found (calculated for $C_{10}H_9N_5O_6Cu$): C, 33.7 (33.5); N, 19.2 (19.5); H, 2.55 (2.53)%; IR (nujol mull) 1014 (w, ν_{sym} NO_2), 1251 (s, ν_{asym} NO_2), 1298, (s, N-aryl) 1465 (s, ν_{asym} NO_2) cm^{-1}

[Cu(Prdpa)Cl_2] (37). To a solution of anhydrous $CuCl_2$ (0.2 g, 1.5 mmol) in EtOH (8 ml) was added a solution of **1** (0.31 g, 1.5 mmol) in EtOH (8 ml). The reaction vessel was sealed and the solution was stirred for an hour. The resulting precipitate was collected, dissolved in a minimum volume of hot CH_2Cl_2 and reprecipitated by dropwise addition of hexane until turbitity persisted, followed by refrigeration, to afford 0.47 g (90%) of **37**.

Data: Light green crystals; Analysis: Found (calculated for $C_{13}H_{13}N_3CuCl_2$): C, 43.0 (45.2); N, 11.3 (12.2); H, 3.51 (3.80)%; IR (nujol mull) 1169 (s, N-alkyl), 1317 (s, N-aryl), 1599 (w, C=C) cm^{-1}.

6.5.1.2 Zn(II) Adducts of Rdpa (R = Propenyl)

[Zn(Prdpa)Cl_2] (38). To a solution of anhydrous $ZnCl_2$ (0.33 g, 2.4 mmol) in EtOH (8 ml) was treated with a solution of **1** (0.50 g, 2.4 mmol) in EtOH (8 ml). The reaction vessel was sealed and the solution was stirred for an hour. Thereafter and the resulting precipitate was collected and dissolved in CH_2Cl_2 (10 ml) before being reprecipitated by dropwise addition of cyclohexane followed by refrigeration overnight. On filtration of the resulting solid the reaction yielded 0.65g (86%) of **38**.

Data: Colourless crystals; Analysis: Found (calculated for $C_{13}H_{13}N_3ZnCl_2$): C, 44.7 (45.0); N, 12.1 (12.1); H, 3.75 (3.77)%; ^1H NMR (270 MHz, $CDCl_3$) 4.65 (2H, d, J = 5.13 Hz N-$C\underline{H}_2$), 5.42 (1H, dd, $C\underline{H}_aH_b$=CH), 5.44 (1H, dd, $CH_a\underline{H}_b$=CH), 5.97 (1H, ddt, CH_2-$C\underline{H}$), 7.32 (4H, m, H^2 and H^4), 7.97 (2H, m, H^3), 8.55 (2H, m, H^1); ^{13}C NMR (68 MHz, $CDCl_3$) 54.8 (-$\underline{C}H_2$-N), 116.9 (Ar-$\underline{C}$-H), 120.2 ($\underline{C}H_2$=CH), 120.6 (Ar-$\underline{C}$-H), 131.8 (CH_2=$\underline{C}$H), 141.6 (Ar-$\underline{C}$-H), 147.0 (Ar-$\underline{C}$-H), 155.4 (Ar-$\underline{C}$); IR (nujol mull) 1169 (s, N-alkyl), 1273 (s, N-aryl), 1604 (w, C=C), 2855 (w, alkyl-H) cm^{-1}.

[Zn(Prdpa)(NO_3)$_2$] (39). A solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.30 g, 1.0 mmol) in ethanol (8 ml) was treated with **1** (0.21 g, 1.0 mmol) dissolved in ethanol (8 ml). The sealed

reaction vessel was stirred for an hour and the solution was then concentrated by rotary evaporation. Et_2O was added to initiate precipitation of the product which, after standing overnight at 0°C, was filtered and reprecipitated in a similar manner as before, to yield 0.30 g (73%) of **39**.

Data: Colourless crystals; Analysis: Found (calculated for $C_{13}H_{13}N_5O_6Zn$): C, 38.0 (39.2); N, 17.0 (17.6); H, 3.13 (3.27)%; ^{1}H NMR (270 MHz, $CDCl_3$) 4.64 (2H, d, J = 4.21 Hz, N-C$\underline{H}_2$), 5.38 (1H, dd, C$\underline{H}_a$H$_b$=CH), 5.42 (1H, dd, CH$_a\underline{H}_b$=CH), 5.88 (1H, ddt, CH$_2$-C$\underline{H}$), 7.32 (4H, m, H^2 and H^4), 7.99 (2H, m, H^3), 8.49 (2H, m, H^1); ^{13}C NMR (100 MHz, $CDCl_3$) 55.6 ($\underline{C}H_2$-N), 117.1 (Ar-$\underline{C}$-H), 120.4 ($\underline{C}H_2$=CH), 120.7 (Ar-$\underline{C}$-H), 131.5 (CH$_2$=$\underline{C}$H), 142.0 (Ar-$\underline{C}$-H), 147.3 (Ar-$\underline{C}$-H), 156.0 (Ar-$\underline{C}$); IR (nujol mull) 1008 (w, ν_{sym} NO_2) 1169 (s, N-alkyl), 1271 (w, ν_{sym} NO_2), 1491 (s, ν_{asym} NO_2), 1604 (w, C=C) cm^{-1}.

6.5.1.3 Other Cu(II) Adducts

[Cu(Pedpa)$_2$(NO$_3$)$_2$] (40) and [Cu(Pedpa)(NO$_3$)$_2$] (41). To a solution of $Cu(NO_3)_2{\cdot}3H_2O$ (0.24 g, 1.28 mmol) in MeOH (10 ml) was added a solution of **02** (0.30 g, 1.26 mmol) in MeOH (8 ml). The solution was stirred for 1 h and treated with a small quantity of Et_2O (3 ml) before standing at 0°C overnight. The heterogeneous solid that precipitated was isolated by filtration and added to CH_2Cl_2 (10 ml). The insoluble purple solid that remained was isolated by filtration and washed with Et_2O to yield 0.06 g (7%) of **40**. Cyclohexane was added dropwise to the CH_2Cl_2 filtrate until turbidity just persisted. Refrigeration overnight yielded a blue precipitate, which was isolated by filtration and washed with Et_2O to yield 0.20 g (39%) of **41**.

[Cu(Pedpa)$_2$(NO$_3$)$_2$]. Data: Purple crystals. Analysis: Found (calculated for $C_{30}H_{34}N_8O_6Cu$): C, 53.6 (54.1); N, 16.8 (16.8); H, 5.19 (5.14)%; IR (nujol mull) 1024 (w, ν_{sym} NO_2), 1165 (s, N-alkyl), 1288 (s, N-aryl), 1293 (s, ν_{sym} NO_2), 1460 (s, ν_{asym} NO_2), 1604 (s, C=C stretch) cm^{-1}.

[Cu(Pedpa)(NO$_3$)$_2$]. Data: Dark blue crystals. Analysis: Found (calculated for $C_{15}H_{17}N_5O_6Cu$): C, 42.2 (42.2); N, 16.2 (16.4); H, 4.06 (4.01)%; IR (nujol mull) 1029 (w, ν_{sym} NO_2) 1166 (s, N-alkyl), 1285 (w, ν_{sym} NO_2), 1288 (s, N-aryl), 1460 (w, ν_{asym} NO_2), 1604 (s, C=C stretch) cm^{-1}.

[Cu(Prbmpa)$(NO_3)_2$] (42). A stirred solution of $CuNO_3 \cdot 3H_2O$ (0.13 g, 0.69 mmol) in EtOH (8 ml) was treated with a solution of **4** (0.16 g, 0.69 mmol) in EtOH (8 ml). Stirring was continued for 1 h after which time a blue solid had precipitated. This was collected by filtration and washed with Et_2O before being dissolved in CH_2Cl_2 (10 ml). Cyclohexane was added dropwise until turbitity just persisted and the suspension was held at 0°C overnight to effect full reprecipitation of the solid. On filtration of the solid and 0.19 g (74%) of **42** was isolated.

Data: Blue crystals. Analysis: Found (Calculated for $C_{15}H_{17}N_5O_6Cu$): C, 41.6 (42.2); H, 3.97 (4.01); N, 15.6 (16.4); IR (nujol mull) 1028 (w, ν_{sym} NO_2), 1279 (s, ν_{asym} NO_2), 1456 (s, ν_{asym} NO_2) cm^{-1}.

[Cu(Mamp)Cl_2] (43). To a solution of anhydrous $CuCl_2$ (0.20 g 1.50 mmol) in EtOH (10 ml) was added a solution of **5** (0.25 g 1.50 mmol) dissolved in EtOH (5 ml). The reaction mixture was stirred for 1h and the blue precipitate that formed was isolated and reprecipitated in a similar fashion as before to yield 0.18 g (40%) of **43.**

Data: Dark blue crystals; Analysis: Found (calculated for $C_9H_{14}N_2OCuCl_2$): C, 35.5 (36.0); N, 8.89 (9.32); H, 4.66 (4.69)%; IR (nujol mull) 1190 (s, N-alkyl), 1374 (s, N-aryl), 1558 (w, C=C), 3250 (br, OH) cm^{-1}.

6.5.2 Complexes of R_3tacn (R = Propenyl or Pentenyl).

[Cu(Pr_3tacn)$(NO_3)_2$] (44). A solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.48 g, 2.0 mmol) in MeOH was treated with **28** (0.5 g, 2.0 mmol) in MeOH and the resulting solution stirred overnight at room temperature. Addition of a little Et_2O produced on standing a dark blue solid which was collected and reprecipitated as before to yield 0.47 g (54%) of **44.**

Data: Blue crystals; Analysis: Found (calculated for $C_{15}H_{27}N_5O_6Cu$): C, 41.1 (41.2); H, 6.12 (6.23); N, 15.7 (16.0)%; IR (nujol mull) 1019 (w, ν_{sym} NO_2), 1160 (s, N-alkyl), 1293 (s, ν_{asym} NO_2), 1461 (s, ν_{asym} NO_2), 1603 (w, C=C stretch) cm^{-1}.

[Zn(Pr_3tacn)$(NO_3)_2$] (45). A solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.25 g, 0.84 mmol) in ethanol (8 ml) was treated with **28** (0.21 g, 0.84 mmol) dissolved in ethanol (8 ml). The reaction vessel was sealed and the solution was stirred for an hour. On addition of diethyl ether and

refrigeration overnight a precipitate formed that was isolated by filtration and reprecipitated as before to yield 0.15 g (41%) of **45**.

Data: Colourless crystals; Analysis: Found (calculated for $C_{12}H_{15}N_5O_6Zn$): C, 40.4 (41.1); N, 15.5 (16.0); H, 6.11 (6.20)%; ^{1}H NMR (400 MHz, $CDCl_3$) 2.92 (12H, m, N-C$\underline{H}_2$-C$\underline{H}_2$-N), 3.55 (6H, d, J = 6.82 Hz, N-C$\underline{H}_2$), 5.36 (1H, dd, C$\underline{H}_a$H$_b$=CH), 5.39 (1H, dd, CH$_a\underline{H}_b$=CH), 5.97 (6H, ddt, C$\underline{H}$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 49.8 (N-$\underline{C}$H$_2$-$\underline{C}$H$_2$-N), 60.3 (N-$\underline{C}$H$_2$), 122.9 ($\underline{C}$H), 130.0 ($\underline{C}$H$_2$=) ppm; IR (nujol mull) 1037 (w, ν_{sym} NO_2), 1289 (s, ν_{asym} NO_2), 1456 (s, ν_{asym} NO_2), 1652 (w, C=C) cm^{-1}.

[Cu(Pe$_3$tacn)(NO$_3$)$_2$] (46). This compound was prepared in an analogous manner to the propenyl homologue and after reprecipitation yielded 0.17 g (50%) of **45**.

Data: Blue crystals; Analysis: Found (calculated for $C_{21}H_{39}N_5O_6Cu$): C, 48.4 (47.3); H, 7.5 (7.33); N, 13.0 (13.4)%; IR (nujol mull) 1022 (w, ν_{sym} NO_2), 1286 (s, ν_{asym} NO_2), 1461 (s, ν_{asym} NO_2), 1641 (w, C=C stretch) cm^{-1}.

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Appendix A: Notes on [Cu(Prdpa)$_2$(NO$_3$)$_2$], 34

A crystal of approximate dimensions 0.30 x 0.28 x 0.25 mm was used for data collection. *Crystal data:* $C_{26}H_{26}CuN_8O_6$, M = 610.09, Monoclinic a = 8.850, b = 15.609, c = 9.923 Å, β = 97.357(2)°, U = 1359.5 Å^3, space group $P2_1/a$, Z = 2, D_c = 1.490 Mgm^{-3}, μ(Mo-K$_\alpha$) = 0.860 mm^{-1}, F(000) = 630. Crystallographic measurements were made at 170(2) K on a Nonius Kappa CCD diffractometer in the range $3.19<\theta<27.52°$. Data (17436 reflections) were corrected for Lorentz and polarisation and also for extinction.

In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant.

Analysis of the supramolecular structure revealed that each copper atom is in an octahedral environment.

The solution of the structure (SHELX86)[1] and refinement (SHELX93)[2] converged to a conventional [i.e. 2054 F^2 data with $F_o>4\sigma(F_o)$] R1 = 0.0303 and wR2 = 0.1020. Goodness of fit = 0.793. The max. and min. residual densities were 0.535 and -0.542 eÅ^3 respectively. The symmetric unit (shown in **Figure A.1**) along with the labelling scheme was produced using ORTEX[3]. Final fractional atomic bond distances and angles are given in **Table A.2**.

1 Sheldrick, G.M. *Acta Cryst.* (**1990**), *A46*, 467.

2 Sheldrick, G.M. *SHELXL* (**1993**) a computer programme for crystal structure refinement, University of Göttingham.

3 McArdle, P. *J. Appl. Cryst.* (**1995**), *28*, 65.

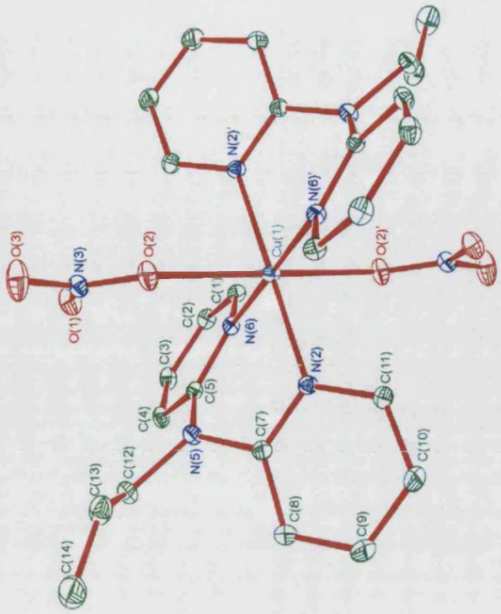

Figure A.1. Molecular structure of [Cu(Prdpa)$_2$(NO$_3$)$_2$].

Empirical formula	$C_{26}H_{26}N_8O_6Cu$
Formula weight	610.09
Temperature	170(2) K
Wavelength	0.71073
Crystal system	Monoclinic
Space group	$P2_1/a$
Unit cell dimensions	a = 8.850 α = 90°
	b = 15.609 β = 97.357(2)°
	c = 9.923 γ = 90°
Volume	1359.5 ^{3}
Z	2
Density (calculated)	1.490 Mg/m^3
Absorption coefficient	0.860 mm^{-1}
F(000)	630
Crystal size	0.30 x 0.28 x 0.25 mm
Theta range for data collection	3.19 to 27.52°
Index ranges	-11<=h<=11; -20<=k<=20; -9<=l<=12
Reflections collected	17436
Independent reflections	3107 [R(int) = 0.0316]
Reflections observed (>2σ)	2981
Max. and min. transmission	0.8137 and 0.7824
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3107 / 0 / 200
Goodness-of-fit in F^2	0.793
Final R indices [I>2σ(I)]	R_1 = 0.0303 wR_2 = 0.1020
R indices (all data)	R_1 = 0.0315 wR_2 = 0.1045
Largest diff. Peak and hole	0.535 and —0.542 e. $^{-3}$

Table A.1. Crystal data and structure refinement for [Cu(Prdpa)$_2$(NO$_3$)$_2$].

Cu(1)-N(6)#1	1.9936(12)	N(6)-C(5)	1.3440(17)
Cu(1)-N(6)	1.9936(12)	N(6)-C(1)	1.3543(17)
Cu(1)-N(2)#1	2.0105(11)	C(1)-C(2)	1.3724(19)
Cu(1)-N(2)	2.0105(11)	C(2)-C(3)	1.401(2)
N(2)-C(7)	1.3391(16)	C(3)-C(4)	1.381(2)
N(2)-C(11)	1.3567(16)	C(4)-C(5)	1.4024(18)
O(1)-N(3)	1.2512(15)	C(7)-C(8)	1.4008(19)
O(2)-N(3)	1.2606(15)	C(8)-C(9)	1.379(2)
O(3)-N(3)	1.2422(16)	C(9)-C(10)	1.390(2)
N(5)-C(7)	1.4040(17)	C(10)-C(11)	1.3771(19)
N(5)-C(5)	1.4055(16)	C(12)-C(13)	1.5029(19)
N(5)-C(12)	1.4719(16)	C(13)-C(14)	1.319(2)
N(6)#1-Cu(1)-N(6)	180.00(6)	O(1)-N(3)-O(2)	120.31(11)
N(6)#1-Cu(1)-N(2)#1	86.07(5)	N(6)-C(1)-C(2)	123.02(13)
N(6)-Cu(1)-N(2)#1	93.93(5)	C(1)-C(2)-C(3)	117.85(13)
N(6)#1-Cu(1)-N(2)	93.93(5)	C(4)-C(3)-C(2)	119.89(13)
N(6)-Cu(1)-N(2)	86.07(5)	C(3)-C(4)-C(5)	118.78(12)
N(2)#1-Cu(1)-N(2)	180.00(6)	N(6)-C(5)-C(4)	121.30(12)
C(7)-N(2)-C(11)	119.43(11)	N(6)-C(5)-N(5)	117.96(11)
C(7)-N(2)-Cu(1)	120.38(9)	C(4)-C(5)-N(5)	120.72(11)
C(11)-N(2)-Cu(1)	120.18(9)	N(2)-C(7)-C(8)	121.10(12)
C(7)-N(5)-C(5)	119.20(10)	N(2)-C(7)-N(5)	117.81(11)
C(7)-N(5)-C(12)	118.66(11)	C(8)-C(7)-N(5)	121.08(12)
C(5)-N(5)-C(12)	117.37(10)	C(9)-C(8)-C(7)	118.79(13)
C(5)-N(6)-C(1)	118.99(12)	C(8)-C(9)-C(10)	120.21(13)
C(5)-N(6)-Cu(1)	120.08(9)	C(11)-C(10)-C(9)	117.99(13)
C(1)-N(6)-Cu(1)	120.75(10)	N(2)-C(11)-C(10)	122.40(13)
O(3)-N(3)-O(1)	120.26(12)	N(5)-C(12)-C(13)	112.09(12)
O(3)-N(3)-O(2)	119.44(12)	C(14)-C(13)-C(12)	123.60(17)

Table A.2. Bond lengths (Å) and angles (°) for [Cu(Prdpa)$_2$(NO)$_2$].

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z

Appendix B: Notes on [Cu(Prdpa)(NO$_3$)$_2$], 35

A crystal of approximate dimensions 0.20 x 0.20 x 0.20 mm was used for data collection. *Crystal data:* $C_{13}H_{13}CuN_5O_6$, M = 398.82, Monoclinic a = 11.942(1), b = 8.719(1), c = 16.123(2) Å, β = 110.26(1)°, U = 1574.9(3) Å^3, space group $P2_1/n$, Z = 4, D_c = 1.682 gcm^{-3}, μ(Mo-K$_\alpha$) = 1.430 mm^{-1}, F(000) = 812. Crystallographic measurements were made at 293(2) K on a CAD4 automatic four-circle diffractometer in the range $2.61<\theta<24.98°$. Data (2659 reflections) were corrected for Lorentz and polarisation and also for extinction.

In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant.

Analysis of the supramolecular structure revealed that each copper atom is in a square pyramidal environment as a consequence of intermolecular bonding to O6.

The solution of the structure (SHELX86)[1] and refinement (SHELX93)[2] converged to a conventional [i.e. 2054 F^2 data with $F_o>4\sigma(F_o)$] R_1 = 0.0264 and wR_2 = 0.0741. Goodness of fit = 1.039. The max. and min. residual densities were 0.322 and -0.328 eÅ^3 respectively. The asymmetric unit (shown in **Figure B.1**) along with the labelling scheme was produced using ORTEX[3]. Final fractional atomic bond distances and angles are given in **Table B.2**.

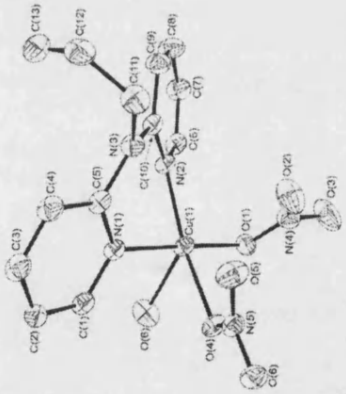

Figure B.1. Molecular structure of [Cu(Prdpa)(NO$_3$)$_2$].

1 Sheldrick, G.M. *Acta Cryst.* (**1990**), *A46*, 467.

2 Sheldrick, G.M. *SHELXL* (**1993**) a computer programme for crystal structure refinement, Universtiy of Göttingham.

3 McArdle, P. *J. Appl. Cryst.* (**1995**), *28*, 65.

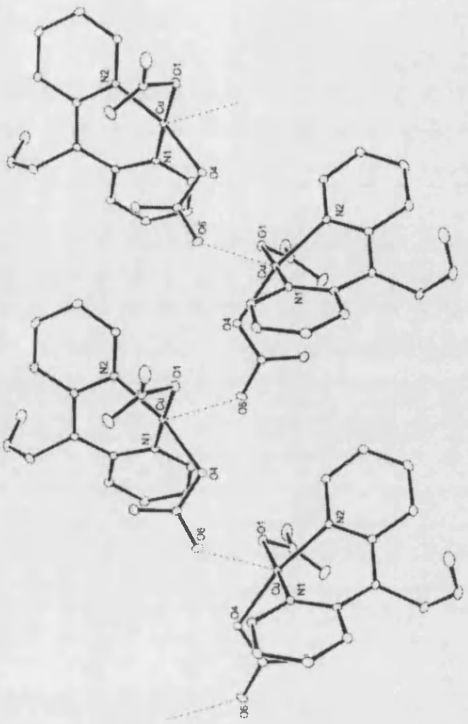

Figure B.2. Extended lattice structure of [Cu(Prdpa)(NO$_3$)$_2$].

Empirical formula	$C_{15}H_{27}CuN_5O_6$
Formula weight	436.96
Temperature	150(2) K
Wavelength	0.71070 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 8.297(0) Å α = 90°
	b = 13.214(0) Å β = 101.917(0)°
	c = 18.057(0) Å γ = 90°
Volume	1937.04(8) Å^3
Z	4
Density (calculated)	1.498 Mg/m^3
Absorption coefficient	1.169 mm^{-1}
F(000)	916
Crystal size	0.13 x 0.10 x 0.10 mm
Theta range for data collection	3.98 to 27.48°
Index ranges	-10<=h<=10; -17<=k<=15; -23<=l<=23
Reflections collected	23874
Independent reflections	4390 [R(int) = 0.0760]
Reflections observed (>2σ)	3456
Absorption correction	Multiscan
Max. and min. transmission	0.8920 and 8.628
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4390 / 0 / 245
Goodness-of-fit in F^2	1.032
Final R indices [I>2σ(I)]	R_1 = 0.0355 wR_2 = 0.0783
R indices (all data)	R_1 = 0.0544 wR_2 = 0.0872
Largest diff. Peak and hole	0.349 and –0.499 e.Å^{-3}

Table B.1. Crystal data and structure refinement for [Cu(Prdpa)(NO$_3$)$_2$.

Cu(1)-O(1)	1.973(0)	C(1)-C(2)	1.504(3)
Cu(1)-O(3)	2.711(2)	C(2)-C(3)	1.320(4)
Cu(1)-O(4)	1.994(9)	C(4)-C(5)	1.520(3)
Cu(1)-N(1)	2.228(7)	C(6)-C(7)	1.496(3)
Cu(1)-N(2)	2.063(9)	C(7)-C(8)	1.312(4)
Cu(1)-N(3)	2.071(3)	C(9)-C(10)	1.523(3)
N(1)-C(15)	1.477(3)	C(11)-C(12)	1.503(3)
N(1)-C(1)	1.487(3)	C(12)-C(13)	1.298(4)
N(1)-C(4)	1.490(3)	C(14)-C(15)	1.525(3)
N(2)-C(6)	1.499(3)	O(1)-N(4)	1.286(3)
N(2)-C(5)	1.499(3)	N(4)-O(2)	1.232(3)
N(2)-C(9)	1.499(3)	N(4)-O(3)	1.232(3)
N(3)-C(10)	1.496(3)	O(4)-N(5)	1.288(3)
N(3)-C(14)	1.501(3)	N(5)-O(6)	1.229(3)
N(3)-C(11)	1.505(3)	N(5)-O(5)	1.232(3)
O(1)-Cu(1)-O(4)	97.68(7)	O(1)-Cu(1)-N(2)	167.27(7)
O(4)-Cu(1)-N(2)	85.34(7)	O(1)-Cu(1)-N(3)	90.79(7)
O(4)-Cu(1)-N(3)	170.81(7)	N(2)-Cu(1)-N(3)	85.63(7)
O(1)-Cu(1)-N(1)	107.91(7)	O(4)-Cu(1)-N(1)	96.27(7)
N(2)-Cu(1)-N(1)	83.93(7)	N(3)-Cu(1)-N(1)	84.44(7)
O(1)-Cu(1)-O(3)	52.17(6)	O(4)-Cu(1)-O(3)	77.87(7)
N(2)-Cu(1)-O(3)	117.10(6)	N(3)-Cu(1)-O(3)	104.88(7)
N(1)-Cu(1)-O(3)	157.17(6)	C(15)-N(1)-C(1)	112.58(17)
C(15)-N(1)-C(4)	113.28(17)	C(1)-N(1)-C(4)	111.64(17)
C(15)-N(1)-Cu(1)	99.95(12)	C(1)-N(1)-Cu(1)	112.60(13)
C(4)-N(1)-Cu(1)	106.09(12)	C(6)-N(2)-C(5)	108.23(17)
C(6)-N(2)-C(9)	110.04(17)	C(5)-N(2)-C(9)	111.37(17)
C(6)-N(2)-Cu(1)	114.51(14)	C(5)-N(2)-Cu(1)	104.24(13)
C(9)-N(2)-Cu(1)	108.34(13)	C(10)-N(3)-C(14)	111.84(17)
C(10)-N(3)-C(11)	109.84(16)	C(14)-N(3)-C(11)	110.00(17)
C(10)-N(3)-Cu(1)	102.75(13)	C(14)-N(3)-Cu(1)	109.16(12)
C(11)-N(3)-Cu(1)	113.10(13)	N(1)-C(1)-C(2)	114.8(2)
C(3)-C(2)-C(1)	124.0(3)	N(1)-C(4)-C(5)	110.99(17)
N(2)-C(5)-C(4)	112.05(17)	C(7)-C(6)-N(2)	112.05(18)
C(8)-C(7)-C(6)	124.2(2)	N(2)-C(9)-C(10)	111.06(17)
N(3)-C(10)-C(9)	109.77(16)	C(12)-C(11)-N(3)	115.25(19)
C(13)-C(12)-C(11)	123.4(3)	N(3)-C(14)-C(15)	112.22(17)
N(1)-C(15)-C(14)	111.70(17)	N(4)-O(1)-Cu(1)	111.71(13)
O(2)-N(4)-O(3)	122.5(2)	O(2)-N(4)-O(1)	118.9(2)
O(3)-N(4)-O(1)	118.51(19)	N(4)-O(3)-Cu(1)	77.49(13)
N(5)-O(4)-Cu(1)	128.78(15)	O(6)-N(5)-O(5)	121.6(2)
O(6)-N(5)-O(4)	117.7(2)	O(5)-N(5)-O(4)	120.6(2)

Table B.2. Bond lengths (Å) and angles (°) for [Cu(Prdpa)(NO$_3$)$_2$].

Appendix C. Notes on [Cu(Hdpa)(NO$_3$)$_2$], 36

A crystal of approximate dimensions 0.13 x 0.08 x 0.05 mm was used for data collection. *Crystal data:* $C_{10}H_9CuN_5O_6$, M = 358.76, Orthorhombic a = 9.6630(2), b = 13.3680(2), c = 20.3340(6) Å, U = 2626.6 Å^3, space group $Pc2_1b$, Z = 8, D_c = 1.814 Mgm^{-3}, μ(Mo-K$_\alpha$) = 1.704 mm^{-1}, F(000) = 1448. Crystallographic measurements were made at 170(2) K on a Nonius Kappa CCD diffractometer in the range $3.65<\theta<26.37°$. Data (27866 reflections) were corrected by applying a multiscan semi-empirical absorption correction (maximum and minimum transmission factors were 1.036 and 0.952 respectively).

In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant.

Analysis of the supramolecular structure revealed that each copper atom is in an octahedral environment.

The solution of the structure (SHELX86)[1] and refinement (SHELX93)[2] converged to a conventional [i.e. 2054 F^2 data with $F_o>4\sigma(F_o)$] R_1 = 0.0580 and wR_2 = 0.1409. Goodness of fit = 1.088. The max. and min. residual densities were 2.009 and -0.757 eÅ^3 respectively. The symmetric unit (shown in **Figure C.1**) along with the labelling scheme was produced using ORTEX[3]. Final fractional atomic bond distances and angles are given in **Tables C.2** and **C.3** respectively.

1 Sheldrick, G.M. *Acta Cryst.* (**1990**), *A46*, 467.

2 Sheldrick, G.M. *SHELXL* (**1993**) a computer programme for crystal structure refinement, University of Göttingham.

3 McArdle, P. *J. Appl. Cryst.* (**1995**), *28*, 65.

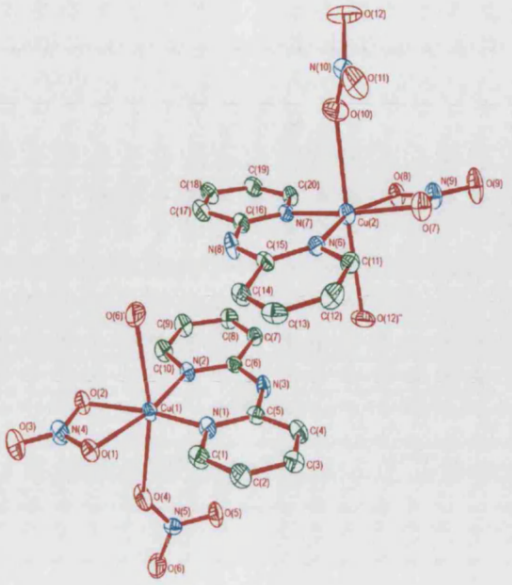

Figure C.1. Structures of the two molecules of [Cu(Hdpa)(NO$_3$)$_2$] per unit cell.

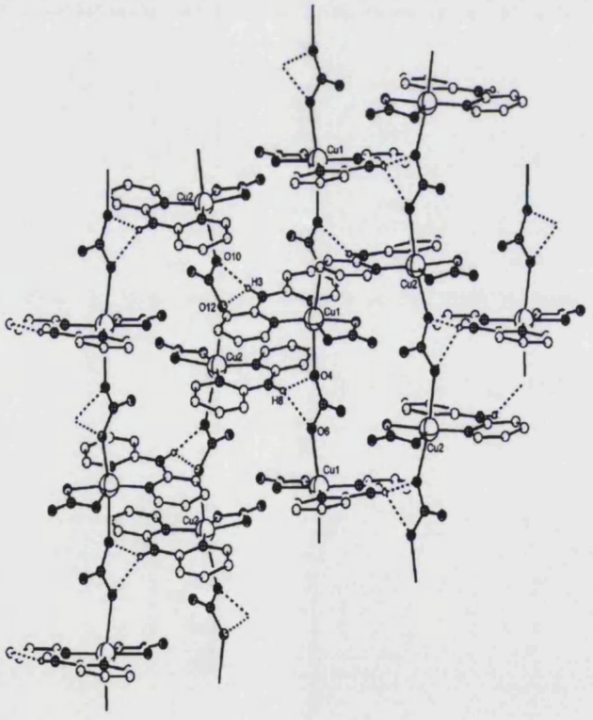

Figure C.2. Extended lattice structure of [Cu(Hdpa)(NO$_3$)$_2$].

Formula weight	358.76
Empirical formula	$C_{10}H_9CuN_5O_6$
Wavelength	0.71070 Å
Crystal system	Orthorhombic
Space group	$P2_1b$
Unit cell dimensions	a = 9.6630(2) Å α = 90°
	b = 13.3680(4) Å β = 90°
	c = 20.3340(6) Å γ = 90°
Volume	2626.6(1) Å^3
Z	8
Density (calculated)	1.814 Mg/m^3
Absorption coefficient	1.704 mm^{-1}
F(000)	1448
Crystal size	0.13 x 0.08 x 0.05 mm
Theta range for data collection	3.65 to 26.37°
Index ranges	-12<=h<=12; -16<=k<=16; -25<=l<=23
Reflections collected	27866
Independent reflections	5217 [R(int) = 0.0675]
Reflections observed (>2σ)	4531
Absorption correction	Multiscan
Max. and min. transmission	
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5217 / 0 / 397
Goodness-of-fit in F^2	1.088
Final R indices [I>2σ(I)]	R_1 = 0.0580 wR_2 = 0.1409
R indices (all data)	R_1 = 0.0699 wR_2 = 0.1478
Absolute structure parameter	0.41(2)
Largest diff. Peak and hole	2.009 and -0.757 e.Å^{-3}

Table C.1. Crystal data and structure refinement for [Cu(Hdpa)(NO$_3$)$_2$].

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N3-H3	0.880	2.104	169.81	2.974	O10 [x, y+1/2, -z-3/2]
N3-H3	0.880	2.446	135.08	3.131	O12 [x, y+1/2, -z-3/2]
N3-H3	0.880	2.699	162.47	3.548	N10 [x, y+1/2, -z-3/2]
N8-H8	0.880	2.167	147.63	2.948	O6 [-x-1, y-1/2, -z-2]
N8-H8	0.880	2.277	155.80	3.100	O4 [-x-1, y-1/2, -z-2]
N8-H8	0.880	*2.628*	*173.03*	3.504	N5 [-x-1, y-1/2, -z-2]

Table C.2 Hydrogen bonds with H..A < r(A) + 2.00Å and <DHA> 110°.

Cu(1)-N2	1.954(5)	N(1)-C(1)	1.357(8)
Cu(1)-N(1)	1.956(5)	N(2)-C(10)	1.342(8)
Cu(1)-O(2)	2.021(4)	N(2)-C(6)	1.346(8)
Cu(1)-O(1)	2.043(5)	N(3)-C(6)	1.375(8)
Cu(1)-O(4)	2.335(5)	N(3)-C(5)	1.383(8)
Cu(1)-N(4)	2.430(6)	N(6)-C(15)	1.324(7)
Cu(1)-O(6)"	2.434(6)	N(6)-C(11)	1.350(8)
Cu(2)-N(7)	1.939(5)	N(7)-C(16)	1.347(7)
Cu(2)-N(6)	1.944(5)	N(7)-C(20)	1.352(7)
Cu(2)-O(7)	2.002(4)	N(8)-C(16)	1.374(7)
Cu(2)-O(8)	2.073(5)	N(8)-C(15)	1.391(8)
Cu(2)-O(10)	2.332(6)	C(1)-C(2)	1.367(9)
Cu(2)-N(9)	2.435(5)	C(2)-C(3)	1.41(1)
Cu(2)-O(12)"	2.448(6)	C(3)-C(4)	1.45(1)
O(1)-N(4)	1.291(7)	C(4)-C(5)	1.380(9)
O(2)-N(4)	1.268(7)	C(6)-C(7)	1.397(8)
O(3)-N(4)	1.201(7)	N(7)-C(8)	1.360(9)
O(4)-N(5)	1.244(9)	C(8)-C(9)	1.39(1)
O(5)-N(5)	1.232(8)	C(9)-C(10)	1.36(1)
O(6)-N(5)	1.227(9)	C(11)-C(12)	1.378(9)
O(6)-Cu(1)'"	2.434(6)	C(12)-C(13)	1.48(1)
O(7)-N(9)	1.287(7)	C(13)-C(14)	1.46(1)
O(8)-N(9)	1.285(7)	C(14)-C(15)	1.417(8)
O(9)-N(9)	1.195(7)	C(16)-C(17)	1.413(9)
O(10)-N(10)	1.267(8)	C(17)-C(18)	1.364(9)
O(11)-N(10)	1.197(8)	C(18)-C(19)	1.49(1)
O(12)-N(10)	1.247(9)	C(19)-C(20)	1.373(8)
N(1)-C(5)	1.357(8)		

Table C.3. Bond lengths (Å) for [Cu(Hdpa)(NO$_3$)$_2$].

N(2)-Cu(1)-N(1)	95.4(2)	N(2)-Cu(1)-O(2)	100.2(2)	C(8)-C(7)-C(6)	119.5(6)
N(1)-Cu(1)-O(2)	163.8(2)	N(2)-Cu(1)-O(1)	163.7(2)	C(10)-C(9)-C(8)	118.0(6)
N(1)-Cu(1)-O(1)	100.9(2)	O(2)-Cu(1)-O(1)	64.5(2)	N(6)-C(11)-C(12)	123.6(6)
N(6)-Cu(1)-N(7)	95.94(22)	N(2)-Cu(1)-O(4)	96.3(3)	C(14)-C(13)-C(12)	119.7(6)
N(1)-Cu(1)-O(4)	102.7(3)	O(2)-Cu(1)-O(4)	79.8(2)	N(6)-C(15)-N(8)	120.9(5)
O(1)-Cu(1)-O(4)	81.5(2)	N(2)-Cu(1)-N(4)	132.7(2)	N(8)-C(15)-C(14)	115.5(5)
N(1)-Cu(1)-N(4)	132.9(2)	O(2)-Cu(1)-N(4)	31.4(2)	N(7)-C(16)-C(17)	120.5(5)
O(1)-Cu(1)-N(4)	32.1(2)	O(4)-Cu(1)-N(4)	78.0(2)	C(18)-C(17)-C(16)	119.5(6)
N(2)-Cu(1)-O(6)'	90.9(3)	N(1)-Cu(1)-O(6)'	87.6(3)	C(20)-C(19)-C(18)	118.9(6)
O(2)-Cu(1)-O(6)'	88.0(2)	O(1)-Cu(1)-O(6)'	88.4(3)	C(7)-C(8)-C(9)	119.3(6)
O(4)-Cu(1)-O(6)'	166.8(2)	N(4)-Cu(1)-O(6)'	88.9(2)	N(2)-C(10)-C(9)	124.0(7)
N(7)-Cu(2)-O(7)	164.8(2)	N(6)-Cu(2)-O(7)	99.2(2)	C(13)-C(12)-C(11)	118.6(6)
N(7)-Cu(2)-O(8)	101.3(2)	N(6)-Cu(2)-O(8)	161.3(2)	C(13)-C(14)-C(15)	117.9(6)
O(7)-Cu(2)-O(8)	63.7(2)	N(7)-Cu(2)-O(10)	83.3(2)	N(6)-C(15)-C(14)	123.6(6)
N(6)-Cu(2)-O(10)	105.2(3)	O(7)-Cu(2)-O(10)	92.5(3)	N(7)-C(16)-N(8)	122.0(5)
O(8)-Cu(2)-O(10)	84.3(2)	N(7)-Cu(2)-N(9)	133.1(2)	N(8)-C(16)-C(17)	117.5(5)
N(6)-Cu(2)-N(9)	130.6(2)	O(7)-Cu(2)-N(9)	32.9(2)	C(17)-C(18)-C(19)	119.5(6)
O(8)-Cu(2)-N(9)	32.9(2)	O(10)-Cu(2)-N(9)	88.4(2)	N(7)-C(20)-C(19)	122.4(6)
N(7)-Cu(2)-O(12)"	94.6(3)	N(6)-Cu(2)-O(12)"	83.0(3)	N(3)-C(6)-C(7)	117.9(5)
O(7)-Cu(2)-O(12)"	87.5(3)	O(8)-Cu(2)-O(12)"	88.2(2)	O(11)-N(10)-O(10)	123.1(6)
O(10)-Cu(2)-O(12)"	171.7(2)	N(9)-Cu(2)-O(12)"	87.2(2)	N(1)-C(1)-C(2)	123.4(6)
N(4)-O(1)-Cu(1)	90.7(3)	N(4)-O(2)-Cu(1)	92.4(4)	C(4)-C(3)-C(2)	119.7(6)
N(5)-O(4)-Cu(1)	131.5(5)	N(5)-O(6)-Cu(1)"'	138.8(5)	N(1)-C(5)-C(4)	121.4(6)
N(9)-O(7)-Cu(2)	93.0(3)	N(9)-O(8)-Cu(2)	89.8(3)	C(4)-C(5)-N(3)	118.3(6)
N(10)-O(10)-Cu(2)	127.2(5)	C(5)-N(1)-C(1)	117.7(5)	N(2)-C(6)-C(7)	121.3(5)
C(5)-N(1)-Cu(1)	124.5(4)	C(1)-N(1)-Cu(1)	117.7(4)	O(11)-N(10)-O(12)	122.6(6)
C(10)-N(2)-C(6)	117.8(2)	C(10)-N(2)-Cu(1)	117.5(4)	O(12)-N(10)-O(10)	114.1(6)
C(6)-N(2)-Cu(1)	124.7(4)	C(6)-N(3)-C(5)	133.8(5)	C(1)-C(2)-C(3)	117.6(7)
O(3)-N(4)-O(2)	124.5(6)	O(3)-N(4)-O(1)	122.1(5)	C(3)-C(4)-C(5)	120.2(6)
O(2)-N(4)-O(1)	113.4(5)	O(3)-N(4)-Cu(1)	178.1(5)	N(1)-C(5)-N(3)	120.2(6)
O(2)-N(4)-Cu(1)	56.2(3)	O(1)-N(4)-Cu(1)	57.2(3)	N(2)-C(6)-N(3)	120.7(5)
O(6)-N(5)-O(5)	125.1(7)	O(6)-N(5)-O(4)	114.7(6)	O(9)-N(9)-O(7)	123.8(6)
O(5)-N(5)-O(4)	120.1(7)	C(15)-N(6)-C(11)	116.5(5)	O(9)-N(9)-Cu(2)	178.3(6)
C(15)-N(6)-Cu(2)	124.7(4)	C(11)-N(6)-Cu(2)	118.2(4)	O(7)-N(9)-Cu(2)	55.2(3)
C(16)-N(7)-C(20)	119.0(5)	C(16)-N(7)-Cu(2)	123.2(4)	O(8)-N(9)-Cu(2)	58.3(3)
C(20)-N(7)-Cu(2)	117.4(4)	C(16)-N(8)-C(15)	131.9(5)		
O(9)-N(9)-O(8)	122.6(6)	O(8)-N(9)-O(7)	113.5(5)		

Table C.4. Bond angles (°) for [Cu(Hdpa)(NO$_3$)$_2$].

Symmetry transformations used to generate equivalent atoms:

#1 -x-1, y-½, -z-2

#2 x, y+½, -z-¾

#3 -x-1, y+½, -z-2

Appendix D: Notes on [Cu(Pr$_3$tacn)(NO$_3$)$_2$], 44

A crystal of approximate dimensions 0.13 x 0.10 x 0.10 mm was used for data collection. *Crystal data:* $C_{15}H_{27}CuN_5O_6$, M = 436.96, Monoclinic a = 8.2970(2), b = 13.2140(3), c = 18.0570(4) Å, β = 101.9170(9)°, U = 1937.04 Å^3, space group $P2_1/c$, Z = 4, D_c = 1.498 Mgm^{-3}, μ(Mo-K$_\alpha$) = 1.169 mm^{-1}, F(000) = 916. Crystallographic measurements were made at 150(2) K on a Nonius Kappa CCD diffractometer in the range $3.98<\theta<27.48°$. Data (23874 reflections) were corrected for Lorentz and polarisation and also for extinction.

In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant.

Analysis of the supramolecular structure revealed that each copper atom is in a square pyramidal environment.

The solution of the structure (SHELX86)[1] and refinement (SHELX93)[2] converged to a conventional [i.e. 2054 F^2 data with $F_o>4\sigma(F_o)$] R_1 = 0.0355 and wR_2 = 0.0783. Goodness of fit = 1.032. The max. and min. residual densities were 0.349 and -0.499 eÅ^3 respectively. The asymmetric unit (shown in **Figure D.1**) along with the labelling scheme was produced using ORTEX[3]. Final fractional atomic bond distances and angles are given in **Table D.2.**

1 Sheldrick, G.M. *Acta Cryst.* (**1990**), *A46*, 467.

2 Sheldrick, G.M. *SHELXL* (**1993**) a computer programme for crystal structure refinement, University of Göttingham.

3 McArdle, P. *J. Appl. Cryst.* (**1995**), *28*, 65.

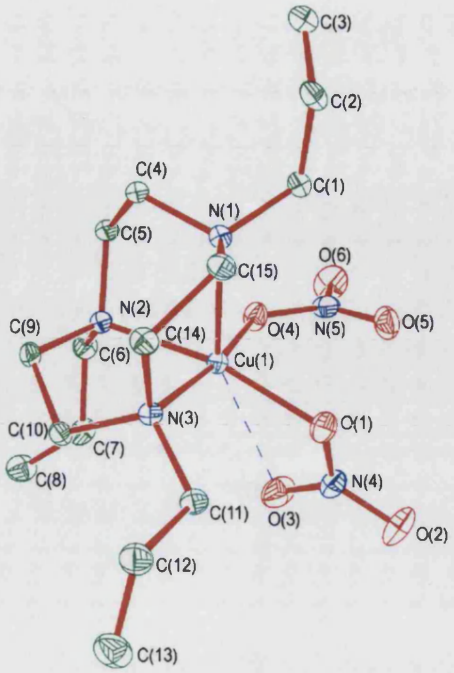

Figure D.1. Molecular structure of [Cu(Pr$_3$tacn)(NO$_3$)$_2$].

Empirical formula	$C_{15}H_{27}CuN_5O_6$
Formula weight	436.96
Temperature	150(2) K
Wavelength	0.71070
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 8.297(0) $\alpha = 90°$
	b = 13.214(0) $\beta = 101.917(0)°$
	c = 18.057(0) $\gamma = 90°$
Volume	1937.04(8) ^{3}
Z	4
Density (calculated)	1.498 Mg/m^3
Absorption coefficient	1.169 mm^{-1}
F(000)	916
Crystal size	0.13 x 0.10 x 0.10 mm
Theta range for data collection	3.98 to 27.48°
Index ranges	-10<=h<=10; -17<=k<=15; -23<=l<=23
Reflections collected	23874
Independent reflections	4390 [R(int) = 0.0760]
Reflections observed (>2σ)	3456
Absorption correction	Multiscan
Max. and min. transmission	0.8920 and 8.628
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4390 / 0 / 245
Goodness-of-fit in F^2	1.032
Final R indices [I>2σ(I)]	$R_1 = 0.0355$ $wR_2 = 0.0783$
R indices (all data)	$R_1 = 0.0544$ $wR_2 = 0.0872$
Largest diff. Peak and hole	0.349 and —0.499 e. $^{-3}$

Table D.1. Crystal data and structure refinement for [Cu(Pr$_3$tacn)(NO$_3$)$_2$].

Cu(1)-O(1)	1.973(0)	C(1)-C(2)	1.504(3)
Cu(1)-O(3)	2.711(2)	C(2)-C(3)	1.320(4)
Cu(1)-O(4)	1.994(9)	C(4)-C(5)	1.520(3)
Cu(1)-N(1)	2.228(7)	C(6)-C(7)	1.496(3)
Cu(1)-N(2)	2.063(9)	C(7)-C(8)	1.312(4)
Cu(1)-N(3)	2.071(3)	C(9)-C(10)	1.523(3)
N(1)-C(15)	1.477(3)	C(11)-C(12)	1.503(3)
N(1)-C(1)	1.487(3)	C(12)-C(13)	1.298(4)
N(1)-C(4)	1.490(3)	C(14)-C(15)	1.525(3)
N(2)-C(6)	1.499(3)	O(1)-N(4)	1.286(3)
N(2)-C(5)	1.499(3)	N(4)-O(2)	1.232(3)
N(2)-C(9)	1.499(3)	N(4)-O(3)	1.232(3)
N(3)-C(10)	1.496(3)	O(4)-N(5)	1.288(3)
N(3)-C(14)	1.501(3)	N(5)-O(6)	1.229(3)
N(3)-C(11)	1.505(3)	N(5)-O(5)	1.232(3)
O(1)-Cu(1)-O(4)	97.68(7)	O(1)-Cu(1)-N(2)	167.27(7)
O(4)-Cu(1)-N(2)	85.34(7)	O(1)-Cu(1)-N(3)	90.79(7)
O(4)-Cu(1)-N(3)	170.81(7)	N(2)-Cu(1)-N(3)	85.63(7)
O(1)-Cu(1)-N(1)	107.91(7)	O(4)-Cu(1)-N(1)	96.27(7)
N(2)-Cu(1)-N(1)	83.93(7)	N(3)-Cu(1)-N(1)	84.44(7)
O(1)-Cu(1)-O(3)	52.17(6)	O(4)-Cu(1)-O(3)	77.87(7)
N(2)-Cu(1)-O(3)	117.10(6)	N(3)-Cu(1)-O(3)	104.88(7)
N(1)-Cu(1)-O(3)	157.17(6)	C(15)-N(1)-C(1)	112.58(17)
C(15)-N(1)-C(4)	113.28(17)	C(1)-N(1)-C(4)	111.64(17)
C(15)-N(1)-Cu(1)	99.95(12)	C(1)-N(1)-Cu(1)	112.60(13)
C(4)-N(1)-Cu(1)	106.09(12)	C(6)-N(2)-C(5)	108.23(17)
C(6)-N(2)-C(9)	110.04(17)	C(5)-N(2)-C(9)	111.37(17)
C(6)-N(2)-Cu(1)	114.51(14)	C(5)-N(2)-Cu(1)	104.24(13)
C(9)-N(2)-Cu(1)	108.34(13)	C(10)-N(3)-C(14)	111.84(17)
C(10)-N(3)-C(11)	109.84(16)	C(14)-N(3)-C(11)	110.00(17)
C(10)-N(3)-Cu(1)	102.75(13)	C(14)-N(3)-Cu(1)	109.16(12)
C(11)-N(3)-Cu(1)	113.10(13)	N(1)-C(1)-C(2)	114.8(2)
C(3)-C(2)-C(1)	124.0(3)	N(1)-C(4)-C(5)	110.99(17)
N(2)-C(5)-C(4)	112.05(17)	C(7)-C(6)-N(2)	112.05(18)
C(8)-C(7)-C(6)	124.2(2)	N(2)-C(9)-C(10)	111.06(17)
N(3)-C(10)-C(9)	109.77(16)	C(12)-C(11)-N(3)	115.25(19)
C(13)-C(12)-C(11)	123.4(3)	N(3)-C(14)-C(15)	112.22(17)
N(1)-C(15)-C(14)	111.70(17)	N(4)-O(1)-Cu(1)	111.71(13)
O(2)-N(4)-O(3)	122.5(2)	O(2)-N(4)-O(1)	118.9(2)
O(3)-N(4)-O(1)	118.51(19)	N(4)-O(3)-Cu(1)	77.49(13)
N(5)-O(4)-Cu(1)	128.78(15)	O(6)-N(5)-O(5)	121.6(2)
O(6)-N(5)-O(4)	117.7(2)	O(5)-N(5)-O(4)	120.6(2)

Table D.2. Bond lengths (Å) and angles (°) for [Cu(Pr$_3$tacn)(NO$_3$)$_2$].

Appendix E: Published Work

PERGAMON

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Syntheses and crystal structures of Cu(II) and Zn(II) complexes of 2,2′-dipyridyl(*N*-propenyl)amine

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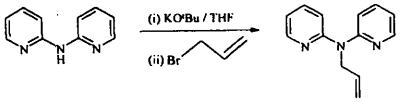
Abstract

Reaction between copper(II)- and zinc(II)-nitrates and 2,2′-dipyridyl(*N*-propenyl)amine (Prdpa) affords 1:1 complexes $M(Prdpa)(NO_3)_2$ (M = Cu, **1**; M = Zn, **5**) for both metal ions and a 1:2 adduct $M(Prdpa)_2(NO_3)_2$ (**2**) for copper only. In ethanol **1** dissociates to form **2** and copper nitrate. X-ray diffraction studies on **1**, **2** and **5**, and on the 2,2′-dipyridylamine (Hdpa) analogue of **1**, $Cu(Hdpa)(NO_3)_2$ (**4**), are reported. The metal centres exhibit square pyramidal (**1**) or distorted octahedral (**2**, **4**, **5**) primary coordination spheres. Bridging nitrate groups linking Cu atoms in **1** and **4** result in –Cu–O–N–O–Cu– chains, which in the case of **4** are extensively cross-linked by N – H···ONO_2 H-bonding into 3D-arrays. Intermolecular C – H···ONO_2 interactions are apparent in the solid-state structure of **2**. The structural effects of replacing the N–H atom on Hdpa by a propenyl group in 6-coordinate Cu(II) complexes are assessed.

Keywords: 2,2′-Dipyridyl(*N*-propenyl)amine; Copper; Zinc; Nitrates; Crystal structures

1. Introduction

The structural diversity of transition metal derivatives of the 2,2′-dipyridylamine ligand (Hdpa) and their potential applications in light-emitting devices have been explored in several recent papers [1]. Both the neutral ligand and its anion $[dpa]^-$ frequently coordinate as simple chelates, but Hdpa can also function as a monodentate ligand and the $[dpa]^-$ anion can bind simultaneously to three metal centres as exemplified by $[M_3(dpa)_4X_2]$, where M = Co [2], Ni [3], Cu [4]; X = halogen. One of the trinuclear Co derivatives has been investigated both structurally and theoretically [5] as the first unambiguous example of a molecule satisfying Parkinson's definition of bond-stretch isomerism [6].



Scheme 1.

Our current interest in the coordinating properties of 2,2′-dipyridylamine and its derivatives arose from our earlier studies on the use of organofunctionalised siloxanes as metal ion supports and reactive membranes [7]. A variety of ligating groups can be conveniently bonded to a siloxane via hydrosilylation of a 1-alkenyl substituent on the ligand, but this procedure is not readily applied to many bidentates containing aromatic N-donor centres, because such bases are not easily modified by the addition of an alkenyl chain. However, the N–H group on Hdpa provides a facile opportunity for N-alkenylation (Scheme 1), so providing a route to siloxane supported N-donors which can be subsequently metallated and used in catalysis.

In view of the notable differences between the coordination modes of Hdpa and its deprotonated derivative $[dpa]^-$, we were interested in exploring any differences between the coordination behaviour of Hdpa and Rdpa

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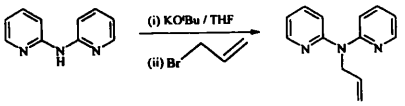
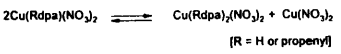


Scheme 2.



Scheme 3.

which might impact on the structures and reactivities of analogous metal complexes, and hence be of relevance to the chemistry of siloxane supported dpa–metal derivatives. In this paper we report on three nitrate complexes of Cu(II) and Zn(II) with Rdpa, where R = *N*-propenyl, and for comparative purposes, one Cu(II)–Hdpa analogue. Copper and zinc ions were selected for this study in view of their importance in a variety of catalytic processes as well as the extreme sensitivity of their coordination geometries to minor changes in ligand environment [8].

2. Results and discussion

2.1. Synthetic considerations

Alkenylation of the secondary amine group in Hdpa was achieved in only low yields (approximately 30%) following the addition of allyl bromide to the deprotonated ligand, and chromatographic separation of the reaction products after quenching. Alkenylation of $[dpa]^-$ at a ring nitrogen or at C(5) is also likely to occur in view of the contributions of canonical forms (II) and (III) to the structure of the anion (Scheme 2), but attempts to isolate and identify a pure ring-substituted derivative were unsuccessful. The use of other deprotonating reagents during the alkenylation of Hdpa did not result in an improved yield of the required product, 2,2′-dipyridyl(*N*-propenyl)amine. We note that 2,2′-dipyridyl(*N*-trimethylsilyl)amine has also been prepared from Hdpa by an analogous procedure, but the product yield was not reported [9].

Metallation of Prdpa with copper nitrate in a 1:1 mole ratio in ethanol produced a low yield of green $Cu(Prdpa)(NO_3)_2$ (**1**) together with purple $Cu(Prdpa)_2(NO_3)_2$ (**2**). A 2:1 mole ratio of ligand to copper nitrate in ethanol afforded **2** only, whereas the former was produced in high yield by using acetone as solvent. Dissolution of **1** in a large excess of ethanol resulted in disproportionation and precipitation of **2**.

It has been noted previously [10] that the reaction of copper(II) nitrate with Hdpa in acetone also produced a green solid, which on recrystallisation from water afforded olive coloured crystals of $Cu(Hdpa)_2(NO_3)_2$ (**3**). As the intermediate green solid was not characterised we have repeated this reaction and shown the green product to be $Cu(Hdpa)(NO_3)_2$ (**4**). This same complex is also conveniently prepared in over 90% yield using methanol as solvent, from which it forms crystals suitable for structural analysis.

For both Hdpa and Prdpa complexes of copper(II) nitrate, facile, solvent dependent ligand exchange occurs (Scheme 3), and either the 1:1 or 2:1 complexes can be isolated in an analytically pure state by judicious choice of conditions.

The analogous reaction between Prdpa and zinc nitrate in ethanol in either 1:1 or 2:1 mole ratio yielded only $Zn(Prdpa)(NO_3)_2$ (**5**), as colourless crystals suitable for X-ray analysis without further purification. ^1H NMR measurements on **5** dissolved in either $CDCl_3$ or CD_3OD revealed a single set of signals for the coordinated ligand, with no indication that the identity of the solution species changed on changing the solvent.

2.2. Crystal structures

Crystal data and relevant experimental parameters used in the structure determinations of **1**, **2**, **4** and **5** are reported in Table 1. Selected bond lengths and angles for all four complexes are listed in Table 2.

Structural analysis of crystals of $Cu(Prdpa)(NO_3)_2$ (**1**) revealed that each copper atom is in an approximately square pyramidal ligand environment (Fig. 1). The basal plane consists of the two N atoms of the pyridyl rings of bidentate Prdpa and two O-donors, O(1) and O(4), from nitrate groups. The apical oxygen atom O(6)′ arises via intermolecular bonding to a nitrate group coordinated to an adjacent Cu centre, so affording a supramolecular structure containing a –Cu–O–N–O–Cu– backbone (Fig. 2). Within the nitrate groups the N–O separations are greater for the strongly coordinated O atoms O(1)–N(4) and O(4)–N(5) (average = 1.272(3) Å) than for the non-coordinated O atoms (average = 1.225(3) Å). Intermolecular bonding of O(6)′ results in an intermediate N(5)–O(6) separation (1.236(2) Å). Both Cu–N separations are typical of those found for the 5-coordinate Cu(II)–Hdpa analogues [11]. Buckling of the bidentate Prdpa ligand produces a dihedral angle between the two pyridyl rings of 54.7° with a C(5)–N(3)–C(10) angle of 124.1(2)°.

A crystal structure determination on $Cu(Prdpa)_2(NO_3)_2$ (**2**) revealed a monomeric unit in which the Cu atom is held in a square planar arrangement of Prdpa N-atoms (average Cu–N separation 2.002(12) Å). The monodentate nitrato ligands are weakly coordinated in axial positions (Cu–O separation = 2.509(3) Å), thus affording an elongated octahedral geometry around the metal ion (Fig. 3). A similar centrosymmetric octahedral geometry has also been reported [12] for

$Cu(Hdpa)_2(NO_3)_2$. Average Cu–N separations in both the Prdpa and Hdpa adducts are very similar, whereas the Cu–O separations at 2.472(2) Å for the Hdpa analogue are significantly shorter than those found in **2** (Table 2). The planar equatorial coordination of the four N-donors of the bidentate ligand is only possible because of the extreme flexibility of the pyridyl rings about the exocyclic N atom, and the angle between the planes of these rings in **2** is 51.6°. This compares with an analogous value of 37.4° in $Cu(Hdpa)_2(NO_3)_2$.

There are two molecules in the unit cell of **4**. The molecular chromophore of both consists of an elongated pseudooctahedral arrangement (Fig. 4) where the N-donor atoms of Hdpa and a bidentate nitrate ligand define the equatorial plane, and axial O-atoms of bridging nitrate groups complete the sixfold coordination. Self-assembly of molecular components via secondary bonding is a common feature of metal complexes containing the Hdpa ligand in combination with oxoanions [12,13], and in **4**, the linked octahedral units exhibit a complex pattern of H-bonding between the Hdpa N–H group and coordinated nitrate ligands (H(3)···O(10) and H(3)···O(12) = 2.10 and 2.44 Å, respectively; H(8)···O(6) and H(8)···O(4) = 2.17 and 2.28 Å, respectively). This results in a 3D array of cross-linked linear chains (Fig. 5). The angle between the pyridyl planes of the Hdpa ligand in **4** is only 12.2°.

Although the stoichiometry of the zinc complex **5** is the same as that of **1**, its structure is very different (Fig. 6). The metal coordination sphere consists of a highly distorted octahedron in which the two bidentate nitrate groups are asymmetrically bound. The Zn–N separations (average 2.041(2) Å) are within the range of internuclear distances typical for other 6-coordinate zinc(II)–Hdpa derivatives [14].

Table 1
Crystal data for compounds **1**, **2**, **4** and **5**

Compound	**1**	**2**	**4**	**5**
Empirical formula	$C_{13}H_{11}N_5OCu$	$C_{26}H_{26}N_8O_6Cu$	$C_{10}H_9CuN_5O_6$	$C_{13}H_{13}N_5O_6Zn$
Formula weight	398.82	610.09	358.76	400.65
Temperature (K)	293(2)	170(2)	170(2)	293(2)
Wavelength (Å)	0.71069	0.71073	0.71070	0.71069
Crystal system	monoclinic	monoclinic	orthorhombic	triclinic
Space group	$P2_1n$	$P2_1/a$	$Pc2_1b$	$P\bar{1}$ (No. 2)
Unit cell dimensions				
a (Å)	11.942(1)	8.850(1)	9.663(2)	7.442 (1)
b (Å)	8.719(1)	15.609(1)	13.368(4)	8.6360(1)
c (Å)	16.123(2)	9.923(1)	20.334(6)	13.131(2)
α (°)				92.61(1)
β (°)	110.26(1)	97.36(1)		90.75(1)
γ (°)				107.27(1)
V (Å^3)	1574.9(3)	1359.5	2626.6(1)	804.7(2)
Z	4	2	8	2
D_{calc} (g cm^{-3})	1.682	1.490	1.814	1.653
Absorption coefficient (mm^{-1})	1.430	0.860	1.704	1.568
$F(000)$	812	630	1448	408
Crystal size (mm)	0.2 × 0.2 × 0.2	0.30 × 0.28 × 0.25	0.13 × 0.08 × 0.05	0.3 × 0.25 × 0.25
θ Range (°)	2.61–24.98	3.19–27.52	3.65–26.37	2.47–23.91
Index ranges	$0 \le h \le 10$; $0 \le k \le 10$; $-19 \le l \le 17$	$-11 \le h \le 11$; $-20 \le k \le 20$; $-9 \le l \le 12$	$-12 \le h \le 12$; $-16 \le k \le 16$; $-25 \le l \le 23$	$-8 \le h \le 0$; $-9 \le k \le 9$; $-14 \le l \le 14$
Reflections collected	2659	17436	27866	2732
Independent reflections	2384 [R_{int} = 0.0181]	3107 [R_{int} = 0.0316]	5217 [R_{int} = 0.0675]	2510 [R_{int} = 0.0123]
Data restraints/parameters	2384 0 227	3107/0/200	5217/0/397	2510/0/227
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0264, wR_2 = 0.0741	R_1 = 0.0303, wR_2 = 0.1020	R_1 = 0.0580, wR_2 = 0.1409	R_1 = 0.0319, wR_2 = 0.0755
R indices (all data)	R_1 = 0.0330, wR_2 = 0.0766	R_1 = 0.0315, wR_2 = 0.1045	R_1 = 0.0699, wR_2 = 0.1478	R_1 = 0.0535, wR_2 = 0.0854
Extinction coefficient	0.0051(9)	0.035(4)		0.0034(15)
Goodness-of-fit	1.039	0.793	1.088	1.117
Largest difference peak and hole (e Å^{-3})	0.322 and −0.328	0.535 and −0.542	2.009 and −0.757	0.345 and −0.486
Flack parameter			0.41(2)	

Table 2
Selected bond lengths (Å) and angles (°) for complexes **1**, **2**, **4** and **5**

Complex 1, Cu(Prdpa)(NO$_3$)$_2$					
Bond distances					
Cu(1)–N(1)	1.961(2)	Cu(1)–N(2)	1.981(2)	Cu(1)–O(1)	1.966(2)
Cu(1)–O(4)	2.010(2)	Cu(1)–O(6)′	2.408(2)		
Bond angles					
N(1)–Cu(1)–N(2)	87.15(8)	N(1)–Cu(1)–O(1)	176.64(8)		
N(2)–Cu(1)–O(1)	93.21(8)	O(1)–Cu(1)–O(4)	88.53(7)		
O(1)–Cu(1)–O(6)′	84.30(8)	O(4)–Cu(1)–O(6)′	76.99(7)		
N(1)–Cu(1)–O(4)	91.86(7)	N(2)–Cu(1)–O(4)	167.14(7)		
N(1)–Cu(1)–O(6)′	92.54(7)	N(2)–Cu(1)–O(6)′	115.86(7)		
Complex 2, Cu(Prdpa)$_2$(NO$_3$)$_2$					
Bond distances					
Cu(1)–N(2)	2.0105(11)	Cu(1)–N(6)	1.9936(12)	Cu–O(2)	2.509(1)
Bond angles [a]					
N(2)–Cu(1)–N(6)	86.07(5)	N(2)–Cu(1)–O(2)	85.35(4)		
N(6)–Cu(1)–O(2)	97.88(4)	N(6)–Cu(1)–N(6)′	93.93(5)		
O(2)–Cu(1)–N(2)′	94.65(4)	O(2)–Cu(1)–N(6)′	97.88(4)		
Complex 4, Cu(Hdpa)(NO$_3$)$_2$					
Bond distances					
Cu(1)–N(1)	1.956(5)	Cu(1)–N(2)	1.954(5)	Cu(1)–O(1)	2.043(5)
Cu(1)–O(2)	2.021(4)	Cu(1)–O(4)	2.335(5)	Cu(1)–O(6)′	2.434(6)
Cu(2)–N(6)	1.944(5)	Cu(2)–N(7)	1.939(5)	Cu(2)–O(7)	2.002(4)
Cu(2)–O(8)	2.073(5)	Cu(2)–O(10)	2.332(6)	Cu(2)–O(12)′	2.448(6)
Bond angles					
N(1)–Cu(1)–N(2)	95.4(2)	N(1)–Cu(1)–O(1)	100.9(2)		
N(1)–Cu(1)–O(4)	102.7(3)	N(1)–O(1)–O(6)′	88.4(3)		
O(1)–Cu(1)–O(2)	63.5(2)	N(2)–Cu(1)–O(2)	100.2(2)		
N(2)–Cu(1)–O(4)	96.3(3)	N(2)–Cu(1)–O(6)′	90.9(3)		
O(4)–Cu(1)–O(6)′	166.8(2)	C(5)–N(3)–C(6)	133.8(5)		
N(6)–Cu(2)–N(7)	95.95(2)	N(6)–Cu(2)–O(7)	99.2(2)		
N(6)–Cu(2)–O(10)	105.2(3)	N(6)–Cu(2)–O(12)′	83.0(3)		
O(7)–Cu(2)–O(8)	63.7(2)	N(7)–Cu(2)–O(8)	101.3(2)		
N(7)–Cu(2)–O(10)	83.3(3)	N(7)–Cu(2)–O(12)′	94.6(3)		
O(10)–Cu(2)–O(12)′	171.7(2)	C(15)–N(8)–C(16)	131.9(5)		
Complex 5, Zn(Prdpa)(NO$_3$)$_2$					
Bond distances					
Zn(1)–N(1)	2.043(2)	Zn(1)–N(3)	2.039(2)	Zn(1)–O(1)	2.055(2)
Zn(1)–O(2)	2.350(3)	Zn(1)–O(4)	2.099(2)	Zn(1)–O(5)	2.279(3)
Bond angles					
N(1)–Zn(1)–N(3)	89.43(10)	N(1)–Zn(1)–O(1)	101.63(10)		
N(1)–Zn(1)–O(2)	90.85(9)	N(1)–Zn(1)–O(4)	103.55(10)		
N(3)–Zn(1)–O(1)	107.50(10)	N(3)–Zn(1)–O(5)	97.16(10)		
N(3)–Zn(1)–O(4)	105.47(10)	C(5)–N(2)–C(6)	121.1(2)		

[a] Primed atoms generated from unprimed atoms by the $-x$, $-y$, $-z$ symmetry operation.

2.3. Structural comparisons

The solid-state structures of a large number of Hdpa complexes containing Cu(II) in combination with anionic co-ligands have been reported, and of these the most relevant for comparative structural purposes are noted in Refs. [11,12]. Two general features are apparent. First, the flexibility of Hdpa already referred to above, permits very large variations in the dihedral angle between the pyridyl rings in order to accommodate the different coordination geometries observed around Cu(II). With increasing dihedral angle the C–$N_{exocyclic}$–C angle tends to decrease, as does the N···N bite of the ligand. The inverse relationship between these first two parameters is apparent for 6-coordinate Cu(II) complexes containing this ligand from the data in Table 3. Secondly, the presence of the secondary N–H group can promote extensive H-bonding to the electronegative anionic co-ligands, leading to complex 3D arrays, as in complex **2**.

The limited structural data presented in this paper suggest that the alkenylated derivative Prdpa exhibits a similar flexibility to that of Hdpa. However, the relationship between pyridyl ring dihedral angle and

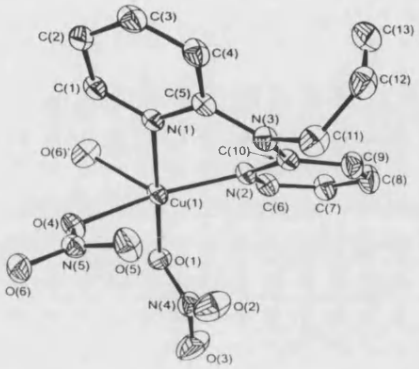


Fig. 1. The solid-state structure of **1** showing the atom labelling scheme. H-atoms are omitted for clarity. Ellipsoids represented at 30% probability level.

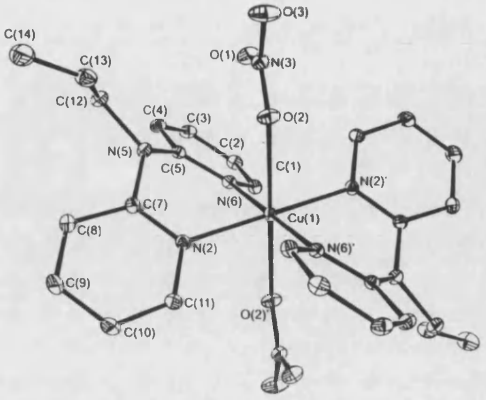


Fig. 3. The molecular structure of **2** showing the atom labelling scheme. H-atoms are omitted for clarity. Ellipsoids represented at 30% probability level.

C–$N_{exocyclic}$–C angle is very different from that shown for analogous complexes of Hdpa (Table 3). In particular the C–$N_{exocyclic}$–C angles for Prdpa in **1** and **2** are very similar to those found in the Hdpa analogues, but the dihedral angles between the pyridyl rings in these two pairs of complexes are much greater for Rdpa than for Hdpa. The data listed in Table 3 also indicate that N-alkenylation of Hdpa has little significant effect on Cu–N separations. The absence of the ligand N–H group might be expected to eliminate H-bonding effects, but for **2** we note an abnormally short contact of 2.47 Å between a H-atom on C(12) and the O-atom of a coordinated nitrate group. The chemical shift of the protons of the methylene group in the free ligand confirm that the $(2\text{-pyridyl})_2N$ moiety is strongly electron withdrawing. Coordination of the Prdpa ligand to a positively charged metal centre is expected to increase the acidity of these protons further, so permitting weak H-bonding under appropriate geometric orientations.

3. Experimental

3.1. General

Solvents for reactions, extractions and chromatography were dried and purified using standard procedures: acetone, ethanol and ethyl acetate (4 Å molecular sieves); diethyl ether and hydrocarbons (sodium/ben-

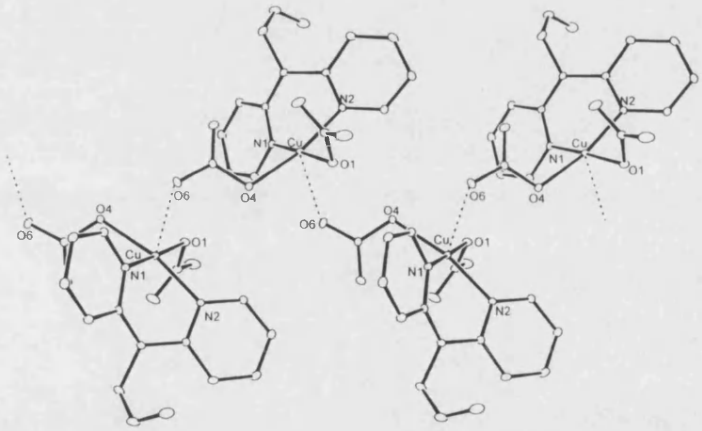


Fig. 2. The supramolecular structure of **1** showing the polymeric Cu–O–N–O–Cu backbone.

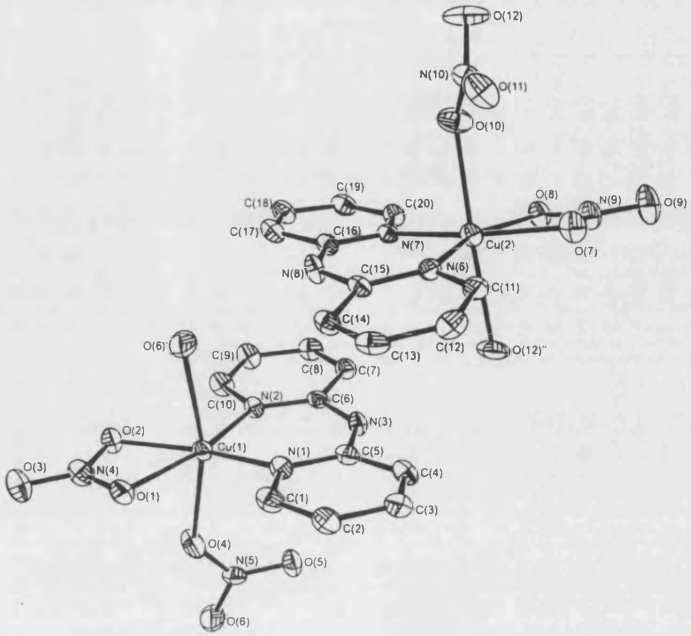


Fig. 4. Disposition of the two molecules of **4** in the unit cell, showing the atom labelling scheme. H-atoms are omitted for clarity.

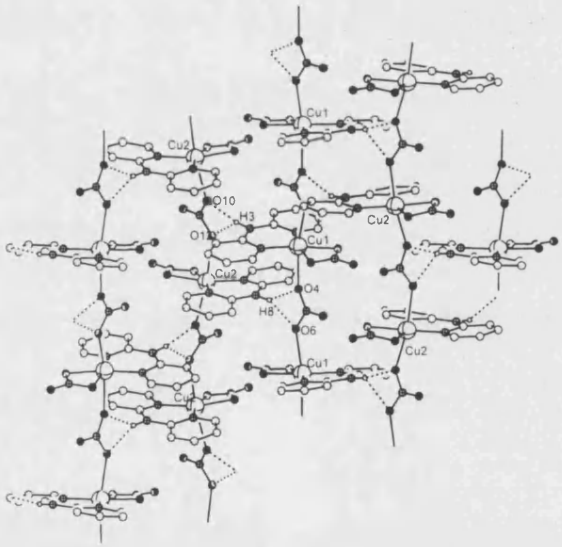


Fig. 5. Packing in the lattice of **4**. The pattern of H-bonding between ligand N–H and coordinated nitrate groups is indicated by dotted lines.

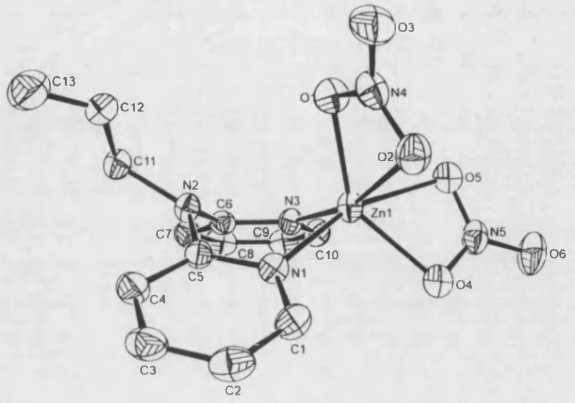


Fig. 6. The molecular structure of **5** showing the atom labelling scheme. H-atoms are omitted for clarity. Ellipsoids represented at 30% probability level.

Table 3
Pyridyl ring dihedral angles, C–$N_{exocyclic}$–C angles and Cu–N separations for 6-coordinate Cu(II) complexes containing Hdpa and Rpda

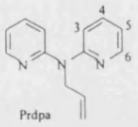
Complex	Dihedral angle (°)	C–$N_{exocyclic}$–C (°)	Cu–N (Å)	Ref.
$Cu(Hdpa)(NO_3)_2$	12.2	133.8	1.956(5), 1.954(5)	This work
$Cu(Hdpa)_2(NO_3)_2$	37.4	122.9 [a]	2.016(2), 2.007(2)	[2]
$[Cu(Hdpa)_2Br_2]\cdot 2H_2O$	39.4	117.5	2.029(5), 1.984(5)	[11d]
$Cu(Hdpa)_2(NCS)_{1.5}(ClO_4)_{0.5}$	40.0	125.0	2.022(3), 2.015(4)	[12]
$Cu(Prdpa)_2(NO_3)_2$	51.6	119.2	2.0105(11), 1.9936(12)	This work
$Cu(Prdpa)(NO_3)_2$	54.7	124.1	1.981(2), 1.961(2)	This work

[a] Average value for the two rings.

zophenone), dichloromethane, chloroform (Na_2SO_4/$MgSO_4$). All other chemicals were used as received. Analytical TLC was carried out using Merck Kieselgel 60F plates. Visualisation was accomplished by UV light, iodine, phosphomolybdic acid or potassium permanganate. Column chromatography was performed using Merck Silica Gel 60 (0.040–0.063 mm).

NMR data were recorded on JEOL GX270 (270.05 MHz ^1H; 67.8 MHz ^{13}C) and EX400 (399.65 MHz ^1H; 100.4 MHz ^{13}C) instruments on $CDCl_3$ solutions unless noted otherwise using TMS as the internal standard. Infrared spectra were recorded on a Nicolet 510P FT-IR instrument, either as a liquid film, or of the solid mulled in Nujol. Elemental CHN analyses were determined by the Analytical Services Unit, University of Bath.

3.2. Preparation of 2,2′-dipyridyl(N-propenyl)amine (Prdpa)



Prdpa

A solution of 2,2′-dipyridylamine (7.67 g, 44.9 mmol) in THF (150 cm^3) was held at 0 °C and treated with KO^{t}Bu (5.03 g, 44.9 mmol). The resulting suspension was stirred for 1 h and then treated dropwise with allyl bromide (3.89 cm^3, 44.9 mmol). After stirring for 1 h solid KBr was filtered from the reaction mixture, and THF removed from the filtrate to leave a yellow oil. The oil was dissolved in dichloromethane (10 cm^3), the solution washed several times with water to remove traces of starting material, and then absorbed onto silica and chromatographed using a 4:1 mixture of hexane and ethyl acetate as the eluent. Solvent was removed from the second fraction from the column, leaving 2.25 g (29%) of the pure product as a light yellow oil. Data: *Anal.* Found: C, 73.3; H, 6.31; N, 19.6. Calc. for $C_{13}H_{13}N_3$: C, 73.9; H, 6.21; N, 19.9%. ^1H NMR (270 MHz, $CDCl_3$): δ 4.86 (d, 2H, N–CH_2), 5.14 (dd, 2H, CH_2=CH–), 6.02 (m, 1H, CH_2=CH–), 6.85 (m, 2H, H^5), 7.16 (d, 2H, H^3), 7.52 (m, 2H, H^4), 8.33 (m, 2H, H^6). ^{13}C NMR (68 MHz, $CDCl_3$): δ 50.3 (–CH_2–N), 114.5 (aromatic), 115.7 (CH_2=CH–), 117.0 (aromatic), 134.7 (CH_2–CH–), 137.2 (aromatic), 148.2 (aromatic), 157.1 (aromatic). IR (liquid film, cm^{-1}): 1151 (s, *N*-alkyl), 1282 (s, *N*-aryl), 1639 (w, C=C), 2855.

3.3. [2,2'-Dipyridyl(N-propenyl)amine]copper(II) nitrate, $Cu(Prdpa)(NO_3)_2$ (1)

To a solution of $Cu(NO_3)_2{\cdot}3H_2O$ (0.57 g, 2.4 mmol) in ethanol (8 cm^3) was added Prdpa (0.50 g, 2.4 mmol) also in ethanol (8 cm^3). The reaction vessel was sealed and the solution was stirred for 1 h resulting in the formation of a purple solid and a green solution. The purple precipitate was removed by filtration, and the filtrate concentrated on a rotary evaporator. Dropwise addition of excess diethyl ether to the filtrate afforded the required product in crude form. The impure product was dissolved in CH_2Cl_2 (approximately 10 cm^3) and the green solution treated with sufficient cyclohexane to start precipitation. On standing at 0 °C dark green crystals of [2,2'-dipyridyl(*N*-propenyl)-amine]copper(II) nitrate (**1**) were formed. Yield: 0.098 g (12%). The same product was isolated in 74% yield when the reaction was carried out using acetone as solvent. *Anal.* Found: C, 39.2; H, 3.10; N, 17.4. Calc. for $C_{13}H_{13}N_5O_6Cu$: C, 39.2; H, 3.28; N, 17.6%. IR (Nujol mull, cm^{-1}): 1008 (w, NO_2 sym stretch), 1161 (s, *N*-alkyl), 1271 (s, NO_2 asym stretch), 1288 (s, *N*-aryl), 1491 (s, NO stretch) 1604 (s, C=C stretch).

3.4. Bis-[2,2'-dipyridyl(N-propenyl)amine]copper(II) nitrate, $Cu(Prdpa)_2(NO_3)_2$ (2)

A solution of $Cu(NO_3)_2{\cdot}3H_2O$ (0.28 g, 1.2 mmol) in ethanol (8 cm^3) was treated dropwise with Prdpa (0.50 g, 2.4 mmol) dissolved in ethanol (8 cm^3). The reaction vessel was sealed and the solution stirred for 1 h at 0 °C after which time purple crystals (0.48 g, 66%) of bis-[2,2'-dipyridyl(*N*-propenyl)amine]copper(II) nitrate (**2**) were isolated by filtration. *Anal.* Found: C, 49.7; H, 4.12; N, 17.8. Calc. for $C_{26}H_{26}N_8O_6Cu$: C, 51.2; H, 4.27; N, 18.4%. IR (Nujol mull, cm^{-1}): 1026 (w, NO stretch), 1163 (s, *N*-alkyl), 1242 (s, NO_2 sym stretch), 1288 (s, *N*-aryl), 1471(s, NO_2 asym stretch) 1601 (s, C=C stretch).

3.5. Bis-(2,2'-dipyridylamine)copper(II) nitrate, $Cu(Hdpa)_2(NO_3)_2$ (3)

This complex was synthesised by a similar method to that given in the literature [10]. To a solution of $Cu(NO_3)_2{\cdot}3H_2O$ (0.24 g, 0.99 mmol) in acetone (8 cm^3) was added 2,2'-dipyridylamine (0.34 g, 1.98 mmol) also in acetone (8 cm^3). The solution was stirred for 1 h after which time the resulting green solid was filtered off and recrystallised from water to afford 0.20 g (38%) of bis(2,2'-dipyridylamine)copper(II) nitrate (**3**). Data: olive green crystals; *Anal.* Found: C, 44.7; H, 3.37; N, 20.8. Calc. for $C_{20}H_{18}N_8O_6Cu$: C, 45.3; H, 3.42; N, 21.1%. IR (Nujol mull, cm^{-1}): 1018 (w, NO stretch), 1269 (s, NO_2 sym stretch), 1288 (s, *N*-aryl), 1468 (s, NO_2 asym stretch).

3.6. (2,2'-Dipyridylamine)copper(II) nitrate, $Cu(Hdpa)(NO_3)_2$ (4)

To a solution of $Cu(NO_3)_2{\cdot}3H_2O$ (1.0 g, 4.14 mmol) in MeOH (10 cm^3) was added a solution of 2,2'dipyridylamine (0.71 g, 4.1 mmol) in MeOH (8 cm^3). The solution was stirred for 1 h and diethyl ether added to complete precipitation of a green solid. This was collected by filtration, washed with diethyl ether, and recrystallised from MeOH to yield 1.39 g (93%) of $Cu(Hdpa)(NO_3)_2$ as a light green solid. *Anal.* Found: C, 33.7; H, 2.55; N, 19.2. Calc. for $C_{10}H_9N_5O_6Cu$: C, 33.5; H, 2.51; N, 19.5%. IR (Nujol mull, cm^{-1}): 1014(w, NO_2 sym stretch), 1251 (s, NO_2 asym stretch), 1298 (s, *N*-aryl), 1465 (s, NO stretch).

3.7. [2,2'-Dipyridyl(N-propenyl)amine]zinc(II) nitrate, $Zn(Prdpa)(NO_3)_2$ (5)

To a solution of $Zn(NO_3)_2{\cdot}6H_2O$ (0.30 g, 1.0 mmol) in ethanol (8 cm^3) was added Prdpa (0.21 g, 1.0 mmol) in ethanol (8 cm^3). After 15 min stirring at room temperature the volume of the solution was reduced by 50% and sufficient diethyl ether added to induced crystallisation. After 48 h at 0 °C, large colourless crystals of the required complex were formed. Yield: 0.30 g (73%). *Anal.* Found: C, 38.0; H, 3.13; N, 17.0. Calc. for $C_{13}H_{13}N_5O_6Zn$: C, 39.2; H, 3.30; N, 17.0%. ^1H NMR (270 MHz, $CDCl_3$): δ 4.64 (d, 2H, $J = 4.2$ Hz, N–CH_2–), 5.40 (t, 2H, $J = 9.9$ Hz, CH_2=CH–), 5.88 (m, 1H, CH_2=C*H*–), 7.32 (m, 4H, H^3 and H^5), 7.99 (m, 2H, H^4), 8.49 (m, 2H, H^6). ^{13}C NMR (68 MHz, $CDCl_3$): δ 55.6 (N–CH_2–), 117.1 (aromatic), 120.4 (*C*H_2=CH), 120.7 (aromatic), 131.5 (CH_2=*C*H–), 142.0 (aromatic), 147.3 (aromatic), 156.0 (aromatic). IR (Nujol mull, cm^{-1}): 1169 (s, *N*-alkyl), 1294 (s, NO_2 asym stretch), 1238 (s, *N*-aryl), 1464 (s, NO stretch), 1604 (w, C=C stretch).

3.8. Crystallography

Crystallographic data for compounds **1**, **2**, **4** and **5** are summarised in Table 1.

Data collections for **1** and **5** were conducted on a CAD4 automatic 4-circle diffractometer, while those for **2** and **4** were implemented on a Nonius Kappa CCD diffractometer. Full matrix anisotropic refinement was implemented in the final least-squares cycles throughout. All data were corrected for Lorentz and polarisation, and with the exception of **4**, for extinction. A multiscan semi – empirical absorption correction was applied to data for **4** (maximum and minimum trans-

mission factors were 1.036 and 0.952, respectively). Hydrogen atoms were included at calculated positions throughout.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 159000–159003, 159309 for compounds **1**, **2**, **4** and **5**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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